



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
01.02.2017 Bulletin 2017/05

(51) Int Cl.:
B29C 49/48 (2006.01) **B29C 49/78** (2006.01)
B29C 49/18 (2006.01) **B29C 49/64** (2006.01)
B29C 49/16 (2006.01) **B29C 49/06** (2006.01)
B29C 49/12 (2006.01) **B29C 49/42** (2006.01)

(21) Application number: **16182977.5**

(22) Date of filing: **15.12.2011**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

- **SCHNEIDER, Mark D.**
St. Charles, IL Illinois 60174 (US)
- **EVINS, Samuel E.**
Olathe, KS Kansas 66061 (US)
- **BOBROV, Sergey, B.**
Aurora, IL Illinois 60504 (US)

(30) Priority: **17.12.2010 US 201061424558 P**
30.09.2011 US 201113250189

(74) Representative: **De Anna, Pier Luigi**
DeAnna-Patent
Schubertstraße 10
80336 München (DE)

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC:
11805341.2 / 2 663 498

(71) Applicant: **Graham Packaging PET Technologies Inc.**
Lancaster, PA 17601 (US)

Remarks:
This application was filed on 05-08-2016 as a divisional application to the application mentioned under INID code 62.

(72) Inventors:
• **SILVERS, Kerry W.**
Campbellsburg, IN Indiana 47208 (US)

(54) **PET CONTAINERS WITH ENHANCED THERMAL PROPERTIES AND PROCESS FOR MAKING SAME**

(57) The process comprises steps of, on an integrated system injecting a molten PET resin into an injection mold cavity to form a preform (22); removing the preform (22) while the preform (22) is at a temperature of from 75° C. to 130° C.; conveying the preform to a conditioning station at a rate such that the temperature of the surface of the preform (22) does not decrease more than 5° C.; conditioning the preform by selectively heating specific areas of the preform (22) comprising at least the neck forming (51, 52), barrel forming (53), heel forming (54), and base forming (55) zones of the preform (22) to achieve a temperature gradient in the specific areas of 20° C; conveying the conditioned preform (22) to a blow mold station at a rate such that the temperature of the surface of the preform does not decrease more than 5° C.

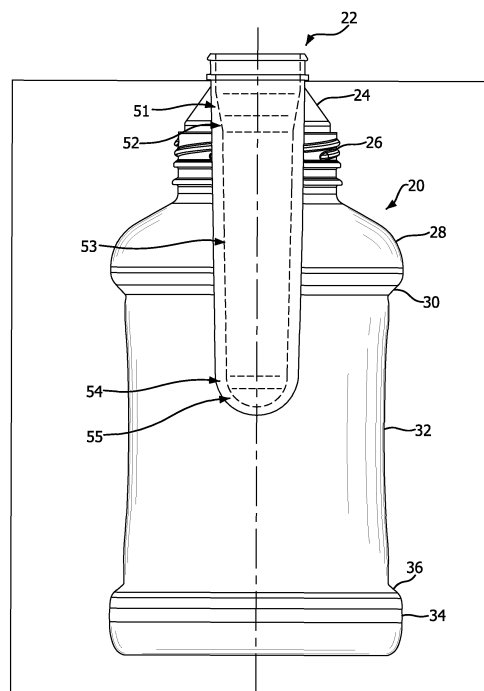


FIG. 2

Description**BACKGROUND OF THE INVENTION**5 **Technical Field of the Invention**

[0001] The present invention relates to a process of manufacturing plastic containers that result in enhanced thermal properties.

10 **[0002]** Plastic containers having enhanced thermal properties allows them to be used in applications where the contents is a fluid, or paste, or solid, or combination of such, and comprises water or water based solutes that is heated up to the boiling point of a fluid, or oil, or oil based recipes that is heated up to 121°C (250°F). Containers having enhanced thermal properties allows them to be used at up to 132°C (270°F) in applications where a filled container is exposed to sterilization, pasteurization or retort processes.

15 **Background Art**

[0003] Blow molding processes for forming PET containers are well known in the art. PET plastic containers have replaced or provided an alternative to glass containers for many applications. However, few food products that must be processed using pasteurization or retort are available in plastic containers. Pasteurization and retort methods are frequently used for sterilizing solid or semi-solid food products, e.g., pickles and sauerkraut. The products may be packed into the container along with a liquid at a temperature less than 82°C (180°F) and then sealed and capped, or the product may be placed in the container that is then filled with liquid, which may have been previously heated, and the entire contents of the sealed and capped container are subsequently heated to a higher temperature. As used herein, "high-temperature" pasteurization and retort are sterilization processes in which the product is exposed to temperatures greater than 80°C.

[0004] Pasteurization and retort differ from hot-fill processing by including heating the filled container to a specified temperature, typically greater than 93°C (200°F), until the contents of the filled container reach a specified temperature, for example 80°C (175°F), for a predetermined length of time. That is, the external temperature of the hot-filled container may be greater than 93°C so that the internal temperature of a solid or semi-solid product reaches approximately 80°C. Retort processes also involve applying overpressure to the container. The rigors of such processing present significant challenges for the use of plastic containers, including containers designed for use in hot-fill processing. For example, during a retort process, when a plastic container is subjected to relatively high temperatures and pressures, the plastic container's shape will distort. Upon cooling, the plastic container generally retains this distorted shape or at least fails to return to its pre-retort shape.

35 **[0005]** Prior art efforts to increase the thermal performance of PET containers have focused on increasing the crystallinity levels of PET. PET is a crystallizable polymer meaning that its crystallinity can be manipulated by the process of forming articles from the PET. These efforts have been successful to the extent of forming PET containers capable of withstanding temperatures up to 97°C (207°F) but not much beyond.

40 **[0006]** A two-phase model of PET morphology states that PET molecules can exist in two phases: an amorphous phase and a crystalline phase. The amorphous phase has been described on a molecular level as resembling a sporadic or chaotic formation that is lack of order. In a solid state the molecule motion belongs to amorphous phase is restricted to very short range vibrations and rotations that is also characterized by a level of energy required to achieve morphing transformation after the distinct energy is delivered. In the molten state there is considerable segmental motion arising from rotation chemical bonds. In the crystalline phase, the polymer chains arrange themselves in the orderly alignment with greater capacity, energy wise. Crystalline portions of the PET molecules can extend straight in one direction and then fold back and forth numerous times to form a folded structure. Numerous such folded structures can stack to form more complex structures known as lamellae. Further crystallized, the lamellae can form globules with even greater energy capacity, but at the cost of being completely opaque.

50 **[0007]** A three-phase model of PET has also been proposed to account for deficiencies observed in the two-phase model. The three phase model includes a (1) crystalline phase, (2) a rigid amorphous phase, and (3) a mobile amorphous phase. One article describing the three-phase model is "Vitrification and Devitrification of the Rigid Amorphous Fraction in poly(ethylene terephthalate)" by Maria Cristina Righetti and Maria Laura Di Lorenzo published at e-polymers.org in 2009.

55 **[0008]** Three commonly known methods for increasing the crystalline fraction of PET include quiescent crystallization, strain-induced crystallization, and a combination thereof. Quiescent crystallization requires exposing an amorphous PET article to heat above the glass transition temperature of PET (70°C or 158°F) at the very slow heating rate to impart mobility into the polymer chains, which allows them to reorganize into a crystalline morphology. This is also known as "cold crystallization." Strain-induced crystallization requires stretching of the PET under proper heat and extension ratios

to orient the PET molecules into an organized matrix. An example of strain-induced crystallization is when a preform (a test tube shaped article) is blown into a mold of greater volume to cause stretching of the preform in a single direction or in multiple directions. Articles with strain-induced crystallinity can be exposed to heat in a process known as heat setting or thermal annealing to cause a relaxation in the stressed-induced crystallinity to increase the thermal properties of the final article. The prior art discloses that the orientation of the polymer chains creates a condition where crystal formation is kinetically favorable upon application of thermal energy. This statement is only applicable to a case where a heated article, for example, loses its transparency as a result of development of heat-induced lamellae and globules.

[0009] Prior art efforts to increase the thermal performance of PET containers have focused on increasing the crystallinity levels of PET. PET is a crystallizable polymer meaning that its crystallinity can be manipulated by the process of forming articles from the PET. These efforts have been successful to the extent of forming PET containers capable of withstanding temperatures up to 97°C (207°F) but not much beyond. The following summarizes such efforts.

[0010] United States Patent Nos. 4,476,170; 4,512,948; 4,522,779; 4,535,025; 4,603,066; 4,713,270; 4,839,127 and 4,891,178 to Jabarin ("the Jabarin patents") disclose single mold systems for forming PET containers. The Jabarin patents disclose using mold temperatures of up to 250°C (482°F) to form containers having crystallinity of up to 60%. Removing the finished containers from such molds without shrinkage of the containers requires either lowering the temperature of the mold to a point where the containers are self-sustaining and can be removed or applying internal pressure to the container when removing the container until the container cools to a temperature where the container is self-sustaining. Neither of these techniques were commercially feasible, however, because the first technique would require extremely long cycle times and the second would be difficult to control in commercial applications.

[0011] United States Patent Nos. 5,562,960 and 5,501,590 disclose two-mold systems for forming PET containers known as a dual-blow system. Those patents require forming an intermediate article in a first mold having a volume greater than the finished container, conveying the intermediate article through a shrink oven to crystallize the intermediate article and then placing the intermediate article into a second mold where it is blown into the finished article. Containers formed from this method have reported crystallinity from 40- 50%.

[0012] United States Patent Nos. 6,485,669; 6,485,670; 6,514,451; 6,749,415 and 6,767,197 ("the Boyd patents") and the Boyd Dissertation disclose that the minimum amount of cooling during the blow molding process and the higher the temperature at de-molding leads to the higher thermal properties of the finished article. The Boyd patents disclose blowing heated air, hot air annealing, or a combination of heated air and fluid onto the inner surface of an article in a blow mold to increase the thermal properties of the finished article.

[0013] Commercial techniques for forming PET utilize both threaded and unthreaded preforms. Preforms are essentially amorphous having less than 5% crystallinity. Upon blow molding a threaded preform into an expanded article the threads will have substantially the same dimension in the finished article as the preform, and, therefore, will have little if any strain induced crystallization. Such a finish will be susceptible to softening and deformation under hot fill conditions. Thus, some amount of crystallization must be imparted to the finish section to enhance thermal performance without shrinking the finish and without imparting whitening to the finish. United States Patent No. 7,033,656 discloses a method for crystallizing the finish section in such a way that one surface is crystallized throughout its length and the other surface includes an area that is essentially uncrystallized with crystallization in a mid-portion of the finish being graded between the surfaces.

[0014] United States Patent No. 4,233,022 discloses an apparatus for forming a PET container from a threaded preform. This patent states that due to the low orientation of the finish and the heel of the container during blow molding that it is undesirable to heat set these areas as it would create whitening in these areas by creating spherulitic crystallinity. Thus, this patent discloses a blow station that selectively heats the strain-oriented sections of the container and cooling the portions of the container having little or no strain orientation.

[0015] United States Patent No. 6,841,117 discloses a method for blow molding a container from a threadless preform. The method includes the step of blow molding a preheated, threadless preform in a heated mold having threads of the desired size to form an intermediate container having threads. The intermediate container has a moil section above the threaded finish which is cut from the intermediate container to form the final container. The finish will have a desired crystallinity of 25% to provide sufficient thermal properties for hot fill applications. More particularly, the preform is preheated to a temperature of 108°C and then disposed within a mold cavity maintained at temperatures from 138 to 143°C. The portion of the mold cavity forming the bottom of the container is maintained at 49 to 54°C. After the mold is closed the preform is blown with air pressure of 40 bar for 1.5 to 3 seconds. A stretch cooling rod blows recirculating cooling gas at a temperature from 20 to 40°C inside the container in the region of the blown threads. The container is removed from the mold at below 80°C.

[0016] Despite these developments, the packaging industry still has to turn to metal or glass containers for applications that require temperatures up to 270°F in applications where a filled container is exposed to sterilization, pasteurization or retort processes. Accordingly, there remains a need to provide PET plastic containers that can withstand such extreme conditions associated with pasteurization and retort processing in order to take advantage of the cost savings that can be realized through manufacture and recycling.

SUMMARY OF THE INVENTION

[0017] In one aspect, the present invention provides a process for forming a blow molded PET plastic container having enhanced thermal properties. The process comprises the steps of, on an integrated system, injecting a molten PET resin into an injection mold cavity to form a preform; removing the preform while the preform is at a temperature of from 75° C. to 130° C.; conveying the preform to at least one conditioning station at a rate such that the temperature of the surface of the preform does not decrease more than 5° C.; conditioning the preform by selectively heating specific areas of the preform comprising at least the neck forming, barrel forming, heel forming, and base forming zones of the preform to achieve a temperature gradient in the specific areas of as much as 20° C; conveying the conditioned preform to a blow mold station at a rate such that the temperature of the surface of the preform does not decrease more than 5° C.; inserting the conditioned preform into a blow mold having walls that define a blow cavity that defines a shape of a finished article, wherein the mold has at least three temperature zones along an axis of the mold all of which are above the glass transition temperature of PET. The at least 3 temperature zones of the mold comprise: zone 1 corresponding to a portion of the mold corresponding to a top portion of the finished container at a temperature of from 73° C. to 120° C.; zone 2 corresponding to a portion of the mold corresponding to a finish portion of the finished container at a temperature of from 160° C. to 240° C.; zones 3 and 5 corresponding to portions of the mold corresponding to a shoulder portion and a heel portion of the finished container at a temperature of from 150° C. to 230° C.; zone 4 corresponding to a portion of the mold corresponding to a barrel portion of the finished container at a temperature of from 190° C. to 250° C.; and zone 6 corresponding to a portion of the mold corresponding to a bottom portion of the finished container at a temperature of from 100° C. to 230° C. The process further comprises blowing the preform into a finished PET container by a stretch blow molding process comprising the steps of

- i. inserting an elongated stretch blow rod into the conditioned preform to contact a bottom portion of the conditioned preform thereby providing a downward pressure to stretch the conditioned preform to a base portion of the mold;
- ii. simultaneously injecting low pressure air into the conditioned preform at a pressure of from 6.89 bar to 13.79 bar (100 psi to 13,8 bars (200 psi)) to form a pre-blown preform; and
- iii. immediately after ii, injecting high pressure air at a pressure of from 27.58 bar to 41.73 bar (27,6 bars (400 psi) to 41,4 bars (600 psi)) into the pre-blown preform to expand the pre-blown preform against the mold walls to form the finished container;
- iii'. holding the finished container in the mold for a time period of from 2 seconds to 20 seconds;
- iv. releasing the finished container from the mold wherein the temperature of the finished container is from 80° C. to 170° C.; and
- iv'. allowing the finished container to cool to ambient temperature.

[0018] According to a further preferred embodiment of the invention the container formed in steps III. and III'. is an intermediated container, and the process further comprises, before steps iv. and iv'., the steps of:

- v. releasing the intermediate container from the mold wherein the temperature of the finished container is from 80° C. to 125° C.;
- vi. conveying the intermediate container to a second mold having walls that define a blow cavity that defines a shape of a finished article and a second volume, wherein the second mold has at least three temperature zones along an axis of the second mold all of which are above the glass transition temperature of PET, wherein the at least 3 temperature zones of the second mold comprise:
 - o zone 1 corresponding to a portion of the mold corresponding to a top portion of the finished container at a temperature of from 73° C. to 120° C.;
 - o zone 2 corresponding to a portion of the mold corresponding to a finish portion of the finished container at a temperature of from 160° C. to 240° C.;
 - o zones 3 and 5 corresponding to portions of the mold corresponding to a shoulder portion and a heel portion of the finished container at a temperature of from 150° C. to 230° C.;
 - o zone 4 corresponding to a portion of the mold corresponding to a barrel portion of the finished container at a temperature of from 190° C. to 250° C.; and
 - o zone 6 corresponding to a portion of the mold corresponding to a bottom portion of the finished container at a temperature of from 100° C. to 230° C, and wherein the second volume is the same as the first volume;
- vii. inserting an elongated stretch blow rod into the intermediate container to contact a bottom portion of the intermediate container thereby providing a downward pressure to stretch the intermediate container to a base portion of the second mold and injecting high pressure air at a pressure of from 27.58 bar to 41.73 bar (400 psi to 41,4 bars

(600 psi)) into the intermediate container to expand the intermediate container against the walls of the second mold to form the finished container;

- viii. directing a cooling fluid to an inner surface of the finished container.

[0019] Further, more preferred embodiment of the invention have been claimed in the appended claims 3-13.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] The foregoing and other features and advantages will be apparent from the following as illustrated in the accompanying drawings wherein like reference numbers generally indicate identical, functionally similar, and/or structurally similar elements.

FIG. 1 is a perspective view of a can-type PET container according to the present invention;

FIG. 2 is a side elevation view showing a preform overlaid onto a mold cavity for a jar-type container of the present invention;

FIG. 3 is a side elevation view of a mold cavity having six zones of temperature control;

FIG. 4 is a side elevation view in cross section of a blow mold station having a blow rod providing recirculating air to an inner surface of the container being formed;

FIG. 5 is a graph of volumetric change versus hot fill temperature for containers having varying crystallinity;

FIGS. 6-10 respectively show a plot of the results of a temperature modulated differential scanning calorimetry data PET containers Sample 3-A, Sample 3-B, Sample 3-C, Sample 1-A and Sample 1-B);

FIG. 11 shows a typical DSC thermogram of PET material forming the shoulder and heel portions of a container according to the present invention;

FIG. 12 shows a typical DSC thermogram of PET material forming the barrel portion of a container according to the present invention;

FIG. 13 is a modulated DSC thermogram for a container sample of the present invention;

FIGS. 14-18 respectively show the X-ray diffraction patterns for Samples 1-A, 1-B, 3-A, 3-B and 3-C;

FIG. 19 shows a portion of X-ray diffraction patterns for the tested samples and vertically spaced from one another for clarity purposes; and

FIG. 20 is a diagram illustrating the tensile strength versus elongation characteristics of a PET container made according to the present invention compared to a prior art heat-set PET container.

DETAILED DESCRIPTION OF THE INVENTION

[0021] Embodiments are discussed in detail below. In describing embodiments, specific terminology is employed for the sake of clarity. While specific exemplary embodiments are discussed, it should be understood that this is done for illustration purposes only. A person skilled in the relevant art will recognize that other components and configurations can be used.

[0022] The present invention provides a container made of a poly(ethylene)terephthalate (PET), having enhanced thermal properties while still providing a container with high clarity. Suitable polyester resins include, for example, homopolymers of poly(ethylene)-phthalate, copolymers of poly(ethylene)terephthalate, poly(ethylene)isophthalate, poly(ethylene)naphthalate, and poly(dimethylene)terephthalate, poly(butylene)terephthalate. In preferred embodiments, the containers of the present invention comprise PET. Preferably, the PET has an intrinsic viscosity of from 0.72 dL/g to 0.86 dL/g. Suitable PET resins include bottle grade PET resins such as, for example, any of the PARASTAR® resins sold by the Eastman Chemical Company, and CLEAR TUF® resins sold by &G Polymers.

[0023] The PET containers of the present invention can have any geometry, shape or size. For example, PET containers according to the present invention can be round, oval, polygonal, and irregular. Suitable containers can be a jar-type, can-type, carafe, wide mouth and any other type container known to those of ordinary skill in the art. Suitable features of the containers can include pressure absorbing features, grip enhancing features, shoulders, bumpers, finishes, chimes, standing rings, necks and others known to those of ordinary skill in the art. Examples of the shapes of containers according to the present invention are shown in FIGS. 1 and 2. FIG. 1 shows a preferred container of the present invention in the form of a plastic (i.e. PET) can 10, having a generally cylindrical side wall 12, a bottom 14, and an open top 16 circumscribed by a flange section 18. FIG. 2 shows a mold cavity 20

comprising walls and a preform 22 for another embodiment of the present invention. The container defined by the walls of the mold cavity 20 comprises a conical top section 24, a finish section 26, a shoulder section 28, a first bumper section 30, a sidewall or barrel section 32, a bottom section 34 and a second bumper section 36.

Process of the Invention

[0024] The process of the present invention provides a process for producing a PET container having thermal properties unexpectedly superior to prior art heat-set containers.

[0025] The present invention provides a process for forming a blow molded PET plastic container having enhanced thermal properties, the process comprising the steps of, on an integrated system: injecting a molten PET resin into an injection mold cavity to form a preform; removing the preform while the preform is at a temperature of from 75°C to 130°C; conveying the preform to at least one conditioning station at a rate such that the temperature of the surface of the preform does not decrease more than 5°C; conditioning the preform by selectively heating at least one portion of the preform selected from the group consisting of: neck forming portion, barrel forming portion, base forming portion, and heel forming portion, to define a conditioned preform; conveying the conditioned preform to a blow mold station at a rate such that the temperature of the surface of the preform does not decrease more than 5°C; inserting the conditioned preform into a blow mold having walls that define a blow cavity that defines a shape of a finished article, wherein the mold has at least three temperature zones along an axis of the mold all of which are above the glass transition temperature of PET; blowing the preform into a finished PET container by a stretch blow molding process comprising the steps of: i. inserting an elongated stretch blow rod into the conditioned preform to contact a bottom portion of the conditioned preform thereby providing a downward pressure to stretch the conditioned preform to a base portion of the mold; ii. simultaneously injecting low pressure air into the conditioned preform at a pressure of from 6.9 bars (100 psi to 13.8 bars (200 psi)) 13.8 bars to form a pre-blown preform; and iii. immediately after ii, injecting high pressure air at a pressure of from 27.6 bars (400 psi) to 41.4 bars (600 psi) into the pre-blown preform to expand the pre-blown preform against the mold walls to form the finished container; holding the finished container in the mold for a time period of from 2 seconds to 20 seconds; releasing the finished container from the mold wherein the temperature of the finished container is from 80°C to 125°C; and allowing the finished container to cool to ambient temperature.

[0026] In another embodiment, the present invention provides a process for forming a blow molded PET plastic container having enhanced thermal properties, the process comprising the steps of, on an integrated system: injecting a molten PET resin into an injection mold cavity to form a preform; removing the preform while the preform is at a temperature of from 75°C to 130°C; conveying the preform to at least one conditioning station at a rate such that the temperature of the surface of the preform does not decrease more than 5°C; conditioning the preform by selectively heating at least one portion of the preform selected from the group consisting of: neck forming portion, barrel forming portion, base forming portion, and heel forming portion, to define a conditioned preform; conveying the conditioned preform to a first blow mold station at a rate such that the temperature of the surface of the preform does not decrease more than 5°C; inserting the conditioned preform into a first blow mold having walls that define a blow cavity that defines a shape of a finished article and a first volume, wherein the first mold has at least three temperature zones along an axis of the first mold all of which are above the glass transition temperature of PET; blowing the preform into a finished PET container by a stretch blow molding process comprising the steps of: i) inserting an elongated stretch blow rod into the conditioned preform to contact a bottom portion of the conditioned preform thereby providing a downward pressure to stretch the conditioned preform to a base portion of the first mold; ii) simultaneously injecting low pressure air into the conditioned preform at a pressure of from 6.9 bars (100 psi) to 13.8 bars (13.8 bars (200 psi)) to form a pre-blown preform; and iii) immediately after ii, injecting high pressure air at a pressure of from 27.6 bars (400 psi) to 41.4 bars (600 psi) into the pre-blown preform to expand the pre-blown preform against the walls of the first mold to form an intermediate container; iv) holding the intermediate container in the mold for a time period of from 2 seconds to 20 seconds; v) releasing the intermediate container from the mold wherein the temperature of the finished container is from 80°C to 125°C; vi) conveying the intermediate container to a second mold having walls that define a blow cavity that defines a shape of a finished article and a second volume, wherein the second mold has at least three temperature zones along an axis of the second mold all of which are above the glass transition temperature of PET, and wherein the second volume is the same as the first volume; vii) inserting an elongated stretch blow rod into the intermediate container to contact a bottom portion of the intermediate container thereby providing a downward pressure to stretch the intermediate container to a base portion of the first mold and injecting high pressure air at a pressure of from 27.6 bars (400 psi) to 41.4 bars (600 psi) into the intermediate container to expand the intermediate container against the walls of the second mold to form the finished container; viii) directing a cooling fluid to an inner surface of the finished container; ix) releasing the finished container from the second mold, wherein the finished container is at a temperature of from 80°C to 170°C; and x) allowing the finished container to cool to ambient temperature.

[0027] The process of the present invention comprises the step of injecting a molten PET resin into a mold having a cavity to form a preform. Any injection-molding machine can be employed, which is equipped with an injection plunger or a screw, reciprocating extrusion unit or continuously operating extrusion unit, and the polymer is injected into the injection mold through, for example, a nozzle, valve, sprue or gate. Then, the PET flows into the cavity of the injection mold where it is solidified into the preform article for stretch blow molding according to the present invention.

[0028] In a preferred form of the invention, the containers are injection molded on an integrated platform where all

molding and conditioning process steps described herein are conducted in line with no interruptions. As used herein, the term "integrated system" refers to a system where PET containers of the present invention are made by a machine having on the same platform an injection molding station for making preforms and at least one blow molding station for blowing the preform into a finished article. Thus, in such integrated system preforms are made by conventional injection molding and then, while still hot, are carried to a blowing station on the same platform in line. In an integrated system, the preform does not have to be reheated to a preferred orientation temperature from ambient temperature as is typically required for non-integrated platforms. Accordingly, the preform of an integrated system will typically have a single heat history unlike a preform that is formed, cooled and then reheated to the desired orientation temperature and, therefore, has multiple heat histories.

[0029] Preforms made and treated on an integrated platform typically have a minimum thermal gradient across the wall and preferably also have a thermal gradient along the preform body. These thermal gradients aid in achieving controlled preferential orientation of desired sections of the finished article that translates into improved thermal resistance properties of the finished container.

[0030] Embodiments of the present invention that employ an integrated platform also have the benefit that the preforms, because they are not exposed to ambient conditions for any appreciable amount of time, have a low moisture content. This aids in preventing hydrolysis of the PET, which otherwise may seize the polymer chains and release phthalic acid. In a preferred embodiment, the preform maintains moisture content of less than 30 ppm from when it is injection molded to when it is blown into a container.

[0031] Shown in FIG. 2 is an exemplary embodiment of a preform according to the present invention wherein preform 22 comprises distinctive zones each of which corresponds to a distinct area of the finished article. In the embodiment shown in FIG. 2, the preform comprises six distinct zones. Zone 51 is a finish-forming region, zone 52 is a shoulder-forming region, zone 53 is a barrel-forming region, zone 54 is a heel-forming region, and zone 55 is a base-forming region. Preform 22 is amorphous in that the PET polymer chains typically do not form lamellae, globules, or any other known molecular organization and, therefore, do not have a substantial amount of crystalline regions, if any exist at all.

[0032] A preform according to the present invention is designed such that the thickness ratio of the preform to the finished container is an important feature. As used herein, the term "thickness ratio" is defined as the thickness in a zone of the preform responsible for forming a corresponding portion of the container to the thickness of the container in the zone correspondingly formed from the portion of the preform. Preferably, the thickness ratio is within the range between 2.0 to 7.5. In some embodiments, the thickness ratio is within the range between 3.5 to 7.0. In other embodiments, the thickness ratio is within the range between 4.0 to 6.0. Although the thickness ratio is dependent on the design geometry of the container and varies from one section of the container to another, it is also to a large extent, dependent on the intended application. For example, for hot-fill applications, the ratio is preferably between 2.8 and 6.4. For applications where both hot-fill and pasteurization operations will be employed, for example, the ratio is within the range between 3.1 and 4.7, more preferably between 3.6 and 4.9, and even more preferably between 3.9 and 5.2. In one preferred embodiment, for example, the shoulder and upper portion of a heat set container has a thickness ratio of between 3.2 and 3.8, more preferably between 3.4 and 4.2, and most preferably 3.8 and 4.6; the barrel portion of the container measured in the middle of the barrel preferably has a thickness ratio of between 3.6 and 4.3, more preferably between 3.8 and 4.5, and most preferably between 4.0 and 4.8; and the base portion preferably has a thickness ratio of between 2.2 and 2.5, more preferably between 2.4 and 2.8, and most preferably between 2.7 and 3.0.

[0033] The density ratio of the preform to the finished container is also an important feature of the present invention. As used herein, the term "density ratio" is defined as the density of the finished article to the density of the amorphous preform. In some embodiments of the present invention, the density ratio is preferred to be within the range of between 1.025 and 1.049. In other embodiments of the present invention, the density ratio is preferred to be in the range of between 1.035 and 1.049. In still other embodiments of the present invention, the density ratio is preferred to be greater than 1.049. Typically, the greater the density ratio the more enhanced thermal resistance exhibited by the resulting container.

[0034] In accordance with the present invention, the average hoop and axial stretch ratios of the preforms typically vary from 3.0 to 4.0 for the hoop and from 1.1 to 1.5 for the axial. These values, however, are average values and zone-dependent based upon the size and geometry of the container as will be appreciated by those skilled in the art.

[0035] The process of the present invention also comprises the steps of removing the molded preform while the preform is still hot and has a thermal gradient through and along the wall of the preform and transporting the hot preform to at least one conditioning station, preferably within 10 seconds after completion of injection molding. Preferably, the temperature of the preform as it is removed from the injection molding station is from 75°C to 130°C, more preferably from 80°C to 110°C, still more preferably from 90°C to 105°C, and most preferably 100°C.

[0036] In preferred embodiments of the present invention where an integrated system is employed, the preform preferably exhibits a temperature gradient through its wall where the preform is generally hotter on the outside of the wall than on the inside wall and the thermal gradient through the wall is typically not exceeding 5°C.

[0037] In preferred embodiments of the present invention, the preform, while it is being transferred from the injection

molding station to a blow molding station is "conditioned" by further modifying the temperature of select portions of the preform. Such temperature modification can occur at at least one conditioning station comprising a heating or cooling element. In preferred embodiments, the temperature of the performs are further modified by heating or cooling certain of the zones (i.e., portions) of the preform. For example, in one preferred embodiment of the present invention, at least one of the neck forming, barrel forming, heel forming, and base forming zones of the preform are further heated to achieve a temperature gradient in the specific areas of as much as 20°C, more preferably as much as 30°C, and most preferably as much as 40°C. Without intending to be bound by any particular theory, it is believed that such selective conditioning promotes preferential orientation of the polymer during the blow molding process. Heat for the conditioning step may be applied by any means known to those skilled in the art such as, for example, hot air generated by a heat gun, infrared heaters, or combinations thereof. The preferred method for the conditioning step is employing a heat gun or a series of heat guns. In other embodiments, the conditioning step employs an infrared heater or a series of infrared heaters.

[0038] The process of the present invention optionally comprises the step of transporting the preform to a second conditioning station, preferably within 10 seconds after the first conditioning step has been completed. When employed, the second conditioning step preferably heats and/or cools at least one of the neck forming, barrel forming and heel forming zones of the preform to ensure that the temperature gradient through the preform walls is as described above with respect to the first conditioning step.

[0039] Regardless of whether one, two, or more conditioning steps are employed as described above, the process of the present invention further comprises the step of conveying the conditioned preform to a blow mold station, preferably within 10 seconds after the final conditioning is completed, to expand the preform into a container by way of the blow molding process of the present invention. The blow molding process of the present invention comprises the step of inserting a preform into a blow mold, locking the blow mold halves, and blowing air into the preform to biaxially stretch the PET into the container shape defined by the mold. Two embodiments of this process will now be described. The first embodiment is a single blow station process and the second embodiment is a dual blow station process wherein each blow station comprises a blow mold. Single Blow Mold Embodiment

[0040] In single blow mold embodiments of the present invention, the single-heat history preform 22 (FIG. 2) is disposed within a blow mold cavity 20 of a single blow station wherein the temperature of the mold is higher than the glass transition temperature ("T_g") of PET. Preferably, the temperature of the mold is between from 73°C to 250°C, more preferably between from 150°C to 240°C, still more preferably between from 160°C to 230°C, and most preferably between from 160°C to 200°C. The wall of the blow mold defines a blow cavity having a volume for receiving a PET preform from the injection molding station and blowing the preform into an expanded PET article against the blow cavity wall.

[0041] In a preferred embodiment shown in FIG. 3, the mold has more than two zones of thermal control along an axial dimension of the mold where the temperature of each zone can be independently set and controlled within the ranges set forth above. FIG. 3 shows one example of a multi-zone blow mold cavity having six zones that will maintain temperatures in the thinner wall sections at higher temperatures than in the thicker wall sections. For example zone 1 for forming the conical top 61 will typically be maintained within the range of 73°C to 120°C, zone 2 corresponding to the finish 62 will typically be maintained within the range of 160°C to 240°C, zones 3 and 5 corresponding respectively to the shoulder 64 and the heel 48 will typically be maintained within the range of 150°C to 230°C, zone 4 corresponding to the barrel section 46 will typically be maintained within the range of 190°C to 250°C and zone 6 corresponding to the bottom 50 will typically be maintained within the range of 100°C to 230°C. Although the mold cavity of FIG. 3 shows six zones of temperature control, the present invention contemplates providing fewer or greater number of zones including from three to eight or more separate zones of temperature control.

[0042] The mold shown in FIG. 2 has a stationary (i.e., fixed) bottom portion. In certain embodiments of the present invention such as that shown in FIG. 3, for example, the mold has a bottom portion 50 that is mounted for reciprocating translational movement along an axis of the cavity from a first position outward of the cavity to a second position axially inward. It should be understood that although bottom portion 50 does not have to be mounted for movement and can be fixed in place in the molding position. The bottom portion 50 can be of a unitary structure or it can have more than one part such as, for example, a pin and sleeve assembly. Still referring to FIG. 3, bottom portion 50 includes a molding surface 50A for forming a bottom portion of the container and, optionally, a pressure absorbing panel in any form such as those disclosed in commonly assigned co-pending U.S. patent application No. 12/709,302 (U.S. Publication No. 2011/0204067).

[0043] Once in the mold, a stretch blow molding process is employed to form the container of the present invention. In preferred embodiments, the stretch blow molding process of the present invention comprises a pre-blow step immediately followed by a blowing step.

[0044] During the pre-blow process, an elongated rod is inserted into the mold cavity of the heated preform and blows a "puff of pressurized air into the preform at a relatively lower pressure of from 100 psi to 13.8 bars (200 psi) and, preferably 10.35 bars (150 psi). In this pre-blow process, the air is preferably added simultaneously as the rod provides a downward pressure thereby stretching the preform to a base portion of the mold and outward under the low air pressure.

Immediately after the pre-blow process, high pressure air at from 27,6 bars (400 psi) to 41,4 bars (600 psi) is injected into the container through the rod to press an outer surface of the preform into contact with an inner surface of the mold cavity to form the container.

[0045] In embodiments where a single blow mold station is employed, the container will preferably remain in the mold for a time of from 2 seconds to 20 seconds, more preferably from 2 seconds to 15 seconds, more preferably from 2 seconds to 12 seconds, more preferably from 4 seconds to 12 seconds, and most preferably from 6 seconds to 12 seconds.

[0046] Preferably, in the single blow mold embodiment, the temperature of the PET container is from 80°C to 170°C, and more preferably from 100°C to 170°C when it is released from the mold. In this temperature range the container will be hot enough to continue thermal annealing yet rigid enough to stand on its own.

Dual Blow Mold Embodiment

[0047] In another embodiment of the present invention, PET containers having improved thermal properties are made by a dual-blow process that employs two blow stations in series, with each blow station having mold walls defining a cavity. In describing this embodiment, the molds will be referred to as the first blow mold and the second blow mold. Thus, in this embodiment, the present invention provides an integrated system for blow molding a PET container comprising, in line: an injection molding station for forming PET preforms, wherein each of the PET preforms is defined by a sidewall defining a cavity, an end wall, and an open end; a first blow molding station comprising a first mold defining a first blow cavity of a first volume for receiving a PET preform from the injection molding station and blowing the preform into an expanded PET article against the first blow cavity, wherein the temperature of the first mold is higher than the glass-transition temperature of PET; a second blow molding station comprising a second mold defining a second blow cavity having a second volume substantially the same as the first volume for receiving the expanded PET article and blowing the expanded PET article against the second blow cavity to form a PET article, followed by cooling the PET article; and a conveyor for moving the PET preforms to the first blow molding station and the expanded PET articles to the second blow molding station, wherein at least one of the first and second molds has at least three zones of thermal control.

[0048] In this embodiment, the first blow mold can be, and preferably is, the same blow mold as the single blow mold embodiment detailed above (either with or without the translational bottom portion 50 shown in FIG. 3). The first blow mold defines a first blow cavity having a first volume for receiving a PET preform from the injection molding station and blowing the preform into an expanded PET article against the first blow cavity. In preferred embodiments of the present invention, the operation of the first blow mold (e.g., temperature profile, heat zones, time in mold, etc.) is as described above. However, in this embodiment, after the conditioned preform is blown in the first mold of the dual-mold embodiment of the present invention to form an intermediate container, the intermediate container is then immediately conveyed to a second blow mold station where the intermediate container is further blown into a finished container. Significantly, in the process of the present invention, each of the first and second blow molds have a blow cavity of roughly the same size and dimension (i.e., cavity volume). Preferably, the second blow mold cavity is the same volume as the first blow mold cavity.

[0049] Once in the second mold, the intermediate container will experience heated zones in second mold, which may be, and preferably are, the same temperature zones (i.e., settings) as those described above for the first blow mold. The intermediate container is then stretched with another elongated rod and subjected to high pressure air at from 27,6 bars (400 psi) to 41,4 bars (600 psi) to be blown into contact with the inner wall surface of the cavity to form the product container.

[0050] The product container will preferably remain in the second mold for a time of from 2 seconds to 20 seconds, more preferably from 2 seconds to 15 seconds, more preferably from 2 seconds to 12 seconds, more preferably from 4 seconds to 12 seconds, and most preferably from 6 seconds to 12 seconds.

[0051] In preferred embodiments of the present invention, the product container is cooled prior to its ejection from the second mold. To cool the product container, cooling fluid may be directed an inner surface of the sidewall of the second mold and/or directly in the product container. The cooling fluid can be a liquid or a gas but more preferably is a gas. Suitable gasses include air, nitrogen and other suitable gasses known to those of skill in the art. In especially preferred embodiments, the present invention allows for selectively cooling predetermined portions of the inner surface of a freshly blown (i.e., heated) container by directing a flow of cooling fluid with the thicker wall portions receiving more cooling fluid than the thinner wall portions as the container has a sidewall having varying thicknesses along an axial dimension of the container with thinner wall portions and thicker wall portions. For example, referring now to FIG. 4, a preferred form of the invention is shown where the cooling fluid is air and is directed to the inner surface of the product container using a blow rod 40 having air holes 42. The air is preferably at a temperature of less than 50°C and more preferably within the range of 20°C to 50°C and under a pressure from 290 psi to 580 psi for a time from two seconds to six seconds. Holes 42 will have varying area dimensions to provide greater amounts of cooling air to the thicker wall portions and less cooling air to the thinner wall portions.

[0052] In preferred embodiments, the product container is removed from the second mold at a temperature of preferably from 80°C to 170°C, and more preferably from 100°C to 170°C where it is rigid and self-supporting, but having enough

heat energy to continue the annealing process outside the mold. The resulting container will possess an enhanced thermal properties required for the hot-fill, pasteurizable and retortable applications and able to withstand temperatures of the contents up to 250°F and packaging processing temperatures up to 270°F.

[0053] Highlights of the process of the present invention include: one step process with a preform gradient temperature between 105°C and 115°C; containers that have a hoop stretch ratio of less than 3.5 and an axial stretch ratio of less than 1.7; and the process allows for continuing thermal relaxation by ambient cooling upon exiting the hot blow mold, i.e., no frozen-in stresses resulting in a higher onset of shrinkage.

The Container of the Present Invention

[0054] The present invention provides a blow-molded PET container comprising a wall having a density of between 1.370 g/cc and 1.385 g/cc, a heat-induced crystallinity of from 18% to 25%, and a strain-induced crystallinity of from 55% to 75%, wherein the PET container, when filled with a liquid having a temperature of from 100°C to 132°C, will not experience a change in volume of greater than 3%. As illustrated in Table 1, prior art PET containers produced by a conventional cold mold process can be characterized by a substantial amount of mobile amorphous phase and small amount of heat induced crystallinity. In comparison, prior art heat set containers typically exhibit a greater percentage of heat induced crystallinity, i.e., up to 35%, and still the same amount of rigid amorphous fracture as in the cold mold containers. Containers produced by the process of the present invention, however, typically having the same small amount of heat induced crystallinity and mobile amorphous phase but exhibit a high percentage of the rigid amorphous phase, i.e., 60% or greater. By having a greater percentage of the rigid amorphous phase characterized by the presence of tightly packed macromolecules and therefore having lesser amount of the free space and greater enthalpy position required to disintegrate macromolecules formation.

Table 1. Typical Average and Ranges of the PET Polymer Morphosis of Prior Art PET Containers Versus PET Containers Produced by the Processes of the Present Invention

<i>Average Typical Range</i>	Heat Induced Crystallinity, %	Rigid Amorphous Fracture, %	Mobil Amorphous Fracture, %
Prior Art Cold Mold Process	$\frac{23}{10-25}$	$\frac{33}{33-45}$	$\frac{43}{23-45}$
Prior Art Heat Set Process	$\frac{35}{30-35}$	$\frac{32}{30-35}$	$\frac{33}{30-35}$
Process of Invention	$\frac{20}{16-24}$	$\frac{60}{55-70}$	$\frac{20}{19-22}$

[0055] A preferred container of the present invention will have the following physical properties. The container can be filled with a liquid from 100°C to 132°C without experiencing a change in volume of greater than 3%, more preferably less than 2% and most preferably less than 1 %. The container will be optically clear before and after exposure to liquids of such temperatures.

[0056] PET containers of the present invention preferably have a density of between 1.370 g/cc and 1.375 g/cc, more preferably greater than 1.375 g/cc, and most preferably greater than 1.385 g/cc.

[0057] Container samples were made in accordance with the single mold embodiment of the present invention and process parameters summarized in Table 2.

Table 2. Process Parameters

Sample	Description	Blow Time Range (sec)	Air Quench Time Range (sec)	Mold Temp. Range (°C)	Combined Axial and Radial Blow Ratio
1-A&B	Prior art 24 oz heat set container made by two-step process	1.5-2.5	0.1-0.8	90-160	>7
3-A	24 oz Container of present invention	4.0-6.0	2.5-3.0	90-210	5.57
3-B	24 oz Container of present invention	6.0-8.0	2.5-3.0	90 - 210	5.57
3-C	45 oz Container of present invention	10.0-18.0	1.0-4.0	90-210	5.57

[0058] Samples 3A and 3B are 24-ounce jar-type containers and Sample 3-C is a 45 ounce jar-type container prepared from PARASTAR 9000 PET resin sold by Eastman Chemical Company using a CIB-LAB laboratory machine with an integrated platform. The barrel section of these samples constitute 80% of the surface area of the containers. The samples were blown from a preform at a starting temperature of from 103°C to 115°C and having a single heat history. The temperatures of the molds for Samples 3A, 3B, 3C were 180°C, 190°C and 200°C, respectively, measured at the barrel section, for periods respectively of six seconds, eight seconds and twelve seconds. Prior art container PET samples 1A and 1 B were 24 ounce jar-type container in an unfilled, clean state and were representative of containers well known to those of skill in the art.

[0059] PET containers of the present invention exhibit superior thermal properties as measured by the lack of shrinkage when filled with a high temperature liquid. This is illustrated by FIG. 5, which shows a plot of volume change (percent) versus hot fill temperatures for sample containers 3A-3C of the present invention and those of the prior art. The containers were first measured for volume by filling to overflow. The containers were then filled with hot vegetable oil, allowed to sit for five minutes, emptied and measured for volume, and the volume measurement process repeated for six discrete temperatures. The temperatures of the oil in the hot fill process were 104.4°C, 115.5°C, 126.6°C, 137.8°C, 148.9°C and 160°C. The containers were filled allowing for 12.5 mm of headspace. The results of the hot fill tests are shown in FIG. 5 with prior art container samples 1 A and 1 B referred to by reference numeral 80 and container samples of the present invention 3A-3C respectively referred to with numerals 82, 84, 86.

[0060] PET containers of the present invention also exhibit differences in polymer morphology as evidence by the measured transitions and crystallinity. Samples of PET containers of the present invention (Samples 3-A, 3-B, 3-C) and of samples of prior art PET containers 1-A, 1-B) were subjected to temperature modulated differential scanning calorimetry (TMDSC) and analyzed in the temperature range of 0°C to 325°C at a heating rate of 5°C/min. The samples were maintained in an inert nitrogen atmosphere with a flow rate of 50 ml/min. The results of the TMDSC data are shown in the following figures (FIG. 6, Sample 3-A, FIG. 7, Sample 3-B, FIG. 8, Sample 3-C, FIG. 9, Sample 1-A and FIG. 10, Sample 1-B). The information is summarized below in Tables 3 and 4.

TABLE 3. Glass Transition Temperatures of the PET bottle samples.

SAMPLE DESCRIPTION	SPECIMEN #	GLASS TRANSITION TEMPERATURE, °C	
		1 st	2 nd
Sample #1-A (24oz)	1	83.8	
	2	93.3	
	Average	88.6	
Sample #1-B (24oz)	1	86.0	
	2	95.5	
	Average	90.8	
Sample #3-A	1	91.6	149.0

EP 3 124 203 A1

(continued)

SAMPLE DESCRIPTION	SPECIMEN #	GLASS TRANSITION TEMPERATURE, °C	
		1 st	2 nd
(24oz)	2	101.5	133.9
	Average	96.6	141.5
Sample #3-B (24oz)	1	89.0	160.9
	2	90.1	163.7
	Average	89.6	162.3
Sample #3-C (45oz)	1	90.6	171.3
	2	104.6	165.9
	Average	97.6	168.6

Table 4. Melting and Crystallization Data of the PET Bottle Samples

Sample Description	Spec #	Tm Onset (°C)	Tm Offset (°C)	Tm Peak (°C)	Hm 140 °C to 275 °C (J/g)	Hc 140 °C to 275 °C (J/g)	Hm-Hc (J/g)	% Crystallinity
Sample #1-A (24oz)	1	237.7	258.7	249.3	58.0	19.7	38.3	27.4
	2	238.5	255.9	249.9	82.2	36.8	45.4	32.4
	Average	238.1	257.3	249.6	70.1	28.3	41.9	29.9
Sample #1-B (24oz)	1	235.7	259.3	253.1	61.0	18.0	43	30.7
	2	234.6	258.3	252.1	62.3	20.3	42	30.0
	Average	235.2	258.8	252.6	61.7	19.2	42.5	30.4
Sample #3-A (24oz)	1	232.5	253.3	246.9	67.6	34.4	33.2	23.7
	2	231.4	255.2	245.3	74.1	38.0	36.1	25.8
	Average	232.0	255.3	246.1	70.9	36.2	34.7	24.8
Sample #3-B (24oz)	1	228.4	253.4	246.7	84.3	42.6	41.7	29.8
	2	224.1	253.5	246	62.0	26.5	35.5	25.4
	Average	226.3	253.5	246.4	73.2	34.55	38.6	27.6
Sample #3-C (45oz)	1	233.3	258.1	251.6	657	237.7	42	30.0
	2	234.7	258.1	250.6	87.7	37.1	50.6	36.0
	Average	234.0	258.1	251.1	76.7	30.4	46.3	33.0

[0061] The data in Table 3 show that the PET containers of the present invention have a first endothermic transition temperature 108 (FIGS. 6-8) and a second endothermic transition temperature 110 substantially higher than the first endothermic transition temperature. In a preferred form of the invention, the second endothermic transition will be at least 20°C higher than the first endothermic glass transition temperature, more preferably at least 30°C higher, even more preferably at least 40°C higher and most preferably at least 50°C higher. In another preferred form of the invention the second endothermic transition will be at a temperature from 120°C to 180°C, even more preferably from 130°C to 170°C and most preferably from 135°C to 165°C.

[0062] In another preferred form of the invention the first endothermic transition morphosis as well as the second endothermic transition morphosis or an exothermic transition morphosis for a given resin composition such as, for example, ParaStar 9000, are not present at all in the range of between 20°C and 200°C, and are replaced with an oversized melting peak showing an enthalpy change of at least +40 J/g, more preferably between +40 J/g and +46 J/g, yet more preferably between +46 J/g and +54 J/g, and most preferably greater than +54 J/g. For example, FIG. 11 shows

a typical DSC thermogram of PET material forming the shoulder and heel portions of a container according to the present invention. Glass transition and cold crystallization morphosis are absent and an enlarged melting peak has a long low temperature ramp starting at 200°C and having an enthalpy change at 44 J/g. Similarly, FIG. 12 shows a typical DSC thermogram of PET material forming the barrel portion of a container according to the present invention. Glass transition and cold crystallization morphosis are absent and an enlarged melting peak has a long low temperature ramp starting at 175°C and having an enthalpy change at 52 J/g. As used herein, the term "enthalpy change" refers to the amount of energy released (exothermic, negative) or absorbed (endothermic, positive) by the substance when the reaction or molecular change occurs.

[0063] The data also show the change in heat capacity of the glass transition temperature for container samples taken from the barrel section of the container (which constitutes 80% of the surface area of the container) of the present invention is at least less than 0.10 J/g°C (FIG. 13).

[0064] The data also show the enthalpy of the second endothermic transition for container samples of the present invention, if present, is greater than 0.50 J/g, more preferably greater than 1.00 J/g, even more preferably greater than 1.50 J/g and most preferably greater than 2.00 J/g.

[0065] None of the prior art PET container samples tested showed a second endothermic transition in their MDSC plots. Without intending to be bound by any particular theory, the proposed explanation for this observed difference is associated with the morphological architecture of the resin wherein the macromolecules are tightly packed by the forces applied to the polymer during blow molding and inducing strain driven motion of the macromolecules thus preventing them from forming lamellae or globular formations but are grossly stretched in at least two principal directions parallel to the axils of orientation developed during blow molding process.

[0066] Samples of the prior art PET containers and containers of the present invention were subjected to X-ray diffraction analysis. Small sections were cut from each sample and flattened by hand. Each sample was then loaded onto a zero background holder and placed into a Panalytical X'Pert MPD Pro diffractometer using Cu radiation at 54KV/40mA. Scans were run over the range of 10°- 70° with a step size of 0.0158° and a counting time of 250 seconds per step. FIGS. 14-18 respectively show the diffraction patterns for Samples 1-A, 1-B, 3-A, 3-B and 3-C. Peaks 1, 3, 4 and 5 are generally attributable to the crystalline phase and Peak 2 is generally attributable to the amorphous phase. Crystalline peaks have half widths in the range of 0.1 ° to 3° and amorphous peaks have half widths close to 10.

[0067] The crystalline and amorphous peaks shown in FIGS. 14-18 were separated and recorded for each sample in Table 5. Notably, the data show a greater number of crystalline peaks in the container samples of the present invention when compared to those of the prior art container samples. Further, there is a shift in the peak position as shown in FIG. 19 and in Tables 6A and 6B below.

Table 5. % Crystallinity in the PET bottle samples.

	Number of Crystalline Peaks	PET Crystalline	PET Amorphous
#1-A	4	30.9%	69.1%
#1-B	4	31.4%	68.6%
#3-A	6	21.3%	78.7%
#3-B	6	23.6%	76.4%
#3-C	6	19.7%	80.3%

Table 6A. XRD Peak Positions Prior Art Samples

	Peak Positions (°)			
	#1	#3	#4	#5
#1-A	13.03°	25.54°	46.19°	53.03°
#1-B	12.84°	25.43°	46.13°	53.17°

Table 6B. XRD Peak Positions (°) of Container Samples of the present invention

Sample	#1	#2	#3	#5	#6	#7	#8
#3-A	12.90°	17.44°	22.5°	25.76°	42.25°	46.63°	53.26°

(continued)

Sample	#1	#2	#3	#5	#6	#7	#8
#3-B	12.99°	17.44°	22.5°	25.94°	42.25°	46.70°	53.38°
#3-C	12.90°	17.44°	22.5°	25.64°	42.25°	46.49°	53.23°

[0068] In a preferred form of the invention, the XRD peaks characterizing the PET containers of the present invention will show at least five crystalline peaks and even more preferably at least six crystalline peaks (FIGS. 17-19). Crystalline peaks 110 can be distinguished from amorphous peaks 12 by the relative shape of the peaks with the crystalline peaks being tall and narrow and the amorphous peaks being rounded and short. Typically a crystalline peak will have a FWHM of from 1.5° to 3° and an amorphous peak will have a FWHM of 9° to 10°. The term FWHM refers to the breadth of a diffraction peak at half the maximum intensity in radians. Two crystalline peaks or inflection points observed in XRD plots of container samples of the present invention but not found in the prior art container samples were found at nominal values of 17.44° and 42.25°.

[0069] Further, as shown in FIG. 19, the XRD peak positions of the present invention are shifted from those shown in the prior art samples. While the shifts between the prior art Samples Series 1 and those of the present invention Series 3 may not seem large, they are well beyond the typical experimental errors. Of particular note is the fact that some peaks are fixed while others shift by 0.5° or more. The most common experimental error would have caused all of the peaks to shift by the same amount. Since this is not the case here, experimental error can be ruled out as the cause of the shift. The XRD data indicate a difference in the crystalline phase between the prior art container samples and those of the present invention.

[0070] As shown in Tables 5 and 7, the containers of the present invention will have a combination of low crystallinity and high density. In a preferred form of the invention the crystallinity of the container will be from 30%, more preferably less than 28%, even more preferably less than 25%. In another preferred form of the invention the crystallinity will be from 30% to 15%, more preferably from 28% to 18% and most preferably from 25% to 18%. In a preferred form of the present invention, the density will be greater than 1.370 g/cc and more preferably greater than 1.375 g/cc. The density of the prior art container samples and those of the present invention were measured and the results are set forth in Table 6 below.

TABLE 7. Density analysis results of PET bottle sample

Sample Description	Specimen #	Density (g/cc)
Sample #1-A (24oz)	1	1.36
	2	1.37
	Average	1.37
Sample #1-B (24oz)	1	1.36
	2	1.37
	Average	1.37
Sample #3-A (24oz)	1	1.38
	2	1.38
	Average	1.38
Sample #3-B (24oz)	1	1.38
	2	1.38
	Average	1.38
Sample #3-C (45oz)	1	1.38
	2	1.38
	Average	1.38

[0071] PET containers of the present invention are also characterized by lower moisture uptake - as much as 24% lower than containers made by prior art heat set processes. For example, PET containers of the present invention made from ParaStar 9000 resin when exposed to ambient conditions (i.e., 22-27°C and 50% relative humidity), generally reaching equilibrium have a moisture content of from 1850 ppm to 1930 ppm, more preferably less than or equal to 1850 ppm, and most preferably less than or equal to 1780 ppm. When exposed to hot-fill conditions (96°C, 100% RH) and/or pasteurization conditions (98°C, 100% RH), PET containers of the present invention made from ParaStar 9000 resin preferably have a moisture content of from 1780 ppm to 1980 ppm, and most preferably less than or equal to 1780 ppm.

[0072] To determine this, several tests were performed on a 24 oz container made from ParaStar 9000 resin according to the present invention (as detailed above) and on a prior art heat set container. The first test was an ambient test, which involved allowing the containers to equilibrate empty under ambient conditions (i.e., 22-27°C and 50% relative humidity) for 4 days. The second test was a hot-fill simulation test, which involved filling the bottles with 96°C (205°F) tap water (measured at the source) after having been stored under ambient conditions for four days. The containers were flood filled with minimum head space and capped immediately after filling, held for 5 minutes, then cooled with 21 °C (70°F) water in a commercial lab- scale pressure cooker combine. For moisture content analysis, 1" by 2" pieces were cut from the barrel portion of the container where no complicating elements such as ribs or pressure folds were present, specimens were protected from being affected further by the ambient air. Analysis was performed on a Karl Fischer titration analyzer. The results of the moisture content analysis are listed in Tables 8 and 9.

Table 8

Table 8

	Moisture content, mg/g, at ambient conditions		
	Minimum content	Average	Maximum content
Heat Set	2.12	2.30	2.48
ThermaSet	1.78	1.86	1.93
% Difference	19%	24%	28%

Table 9

	Moisture content, mg/g, after hot fill and pasteurization		
	Minimum content	Average	Maximum content
Heat Set	2.14	2.17	2.19
ThermaSet	1.78	1.79	1.82
% Difference	20%	21%	20%

[0073] The results listed in Table 8 show that PET containers made according to the present invention have 24% less moisture than the prior art heat-set containers. Without intending to be bound by particular theory, the low moisture uptake of the PET containers of the present invention is most likely the result of less free volume in the PET network due to the strain induced formation described above.

[0074] PET containers of the present invention having low moisture uptake are also characterized by superior mechanical properties. For example, referring now to FIG. 20, a tensile stress versus elongation diagram is shown for the prior art heat set PET container compared to the PET container of the present invention. FIG. 20 shows that the tensile strength for the PET container of the present invention exposed to ambient conditions varies from 965 bars (14,000 psi) to 1241 bars (18,000 psi), with an average at 1172 bars (17,000 psi). The same material tested after hot fill and pasteurization exhibited a slight increase in tensile strength within the range of between 1103 bars (16,000 psi) and 1379 bars (20,000 psi), with an average at 1172 bars (17,000 psi). The prior art heat set containers exhibited a tensile strength range of from between 965 bars (14,000 psi) and 19,000 psi, with an average of 1103 bars (16,000 psi). After hot fill and pasteurization, the tensile strength range of the prior art heat set containers widened to from 1034 bars (15,000 psi) to 1795 bars (26,000 psi), with an average exceeding 1379 bars (20,000 psi).

[0075] At the same time FIG. 20 shows that the load properties at yield of the PET container according to the present invention exposed to ambient conditions vary from 23.4 kg (52 lbf) to 31.8 kg (70 lbf), with an average of 27.2kg (60 lbf). In comparison, the prior art heat set container deviates between 21.8 kg (48 lbf) and 33.7 kg (73 lbf), with an average of 25.4 kg (56 lbf), thus showing greater deviation (lesser performance stability). The elongation (strain) percent for the

24 oz PET container according to the present invention varies between 145% and 170%, with an average of 160%. In comparison, the 740 cc prior art heat set container exhibits an elongation range of from 75% to 125%, with average of 96%. This shows superior elastic properties of the containers of the present invention that is maintained for a longer period of time compared to the prior art heat set containers. This trend continuous when the materials exposed to the hot fill application and pasteurization. All characteristics were measured in vertical principal direction in accordance to ASTM test method D638.

[0076] The embodiments illustrated and discussed in this specification are intended to teach those skilled in the art the best way known to the inventors to make and use the invention. While the invention is described with respect to a wide mouth container, the function of the panel curvatures according to the invention should work with a standard finish (i.e., not a wide mouth neck with a finish).

Claims

1. A process for forming a blow molded PET plastic container having enhanced thermal properties, the process comprising the steps of, on an integrated system:

- injecting a molten PET resin into an injection mold cavity to form a preform;
- removing the preform while the preform is at a temperature of from 75° C. to 130° C.;
- conveying the preform to at least one conditioning station at a rate such that the temperature of the surface of the preform does not decrease more than 5° C.;
- conditioning the preform by selectively heating specific areas of the preform comprising at least the neck forming, barrel forming, heel forming, and base forming zones of the preform to achieve a temperature gradient in the specific areas of as much as 20° C.;
- conveying the conditioned preform to a blow mold station at a rate such that the temperature of the surface of the preform does not decrease more than 5° C.;
- inserting the conditioned preform into a blow mold having walls that define a blow cavity that defines a shape of a finished article, wherein the mold has at least three temperature zones along an axis of the mold all of which are above the glass transition temperature of PET; wherein the at least 3 temperature zones of the mold comprise:

- o zone 1 corresponding to a portion of the mold corresponding to a top portion of the finished container at a temperature of from 73° C. to 120° C.;
- o zone 2 corresponding to a portion of the mold corresponding to a finish portion of the finished container at a temperature of from 160° C. to 240° C.;
- o zones 3 and 5 corresponding to portions of the mold corresponding to a shoulder portion and a heel portion of the finished container at a temperature of from 150° C. to 230° C.;
- o zone 4 corresponding to a portion of the mold corresponding to a barrel portion of the finished container at a temperature of from 190° C. to 250° C.; and
- o zone 6 corresponding to a portion of the mold corresponding to a bottom portion of the finished container at a temperature of from 100° C. to 230° C.;

- blowing the preform into a finished PET container by a stretch blow molding process comprising the steps of:

- i. inserting an elongated stretch blow rod into the conditioned preform to contact a bottom portion of the conditioned preform thereby providing a downward pressure to stretch the conditioned preform to a base portion of the mold;
- ii. simultaneously injecting low pressure air into the conditioned preform at a pressure of from 6.89 bar to 13.79 bar (100 psi to 200 psi) to form a pre-blown preform; and
- iii. immediately after ii, injecting high pressure air at a pressure of from 27.58 bar to 41.73 bar (400 psi to 600 psi) into the pre-blown preform to expand the pre-blown preform against the mold walls to form the finished container;
- iii'. holding the finished container in the mold for a time period of from 2 seconds to 20 seconds;
- iv. releasing the finished container from the mold wherein the temperature of the finished container is from 80° C. to 170° C.; and
- iv'. allowing the finished container to cool to ambient temperature.

2. The process of claim 1, wherein the container formed in steps III. and III'. is an intermediated container, and the

process further comprises, before steps iv. and iv', the steps of:

• v. releasing the intermediate container from the mold wherein the temperature of the finished container is from 80° C. to 125° C.;

• vi. conveying the intermediate container to a second mold having walls that define a blow cavity that defines a shape of a finished article and a second volume, wherein the second mold has at least three temperature zones along an axis of the second mold all of which are above the glass transition temperature of PET, wherein the at least 3 temperature zones of the second mold comprise:

o zone 1 corresponding to a portion of the mold corresponding to a top portion of the finished container at a temperature of from 73° C. to 120° C.;

o zone 2 corresponding to a portion of the mold corresponding to a finish portion of the finished container at a temperature of from 160° C. to 240° C.;

o zones 3 and 5 corresponding to portions of the mold corresponding to a shoulder portion and a heel portion of the finished container at a temperature of from 150° C. to 230° C.;

o zone 4 corresponding to a portion of the mold corresponding to a barrel portion of the finished container at a temperature of from 190° C. to 250° C.; and

o zone 6 corresponding to a portion of the mold corresponding to a bottom portion of the finished container at a temperature of from 100° C. to 230° C, and wherein the second volume is the same as the first volume;

• vii. inserting an elongated stretch blow rod into the intermediate container to contact a bottom portion of the intermediate container thereby providing a downward pressure to stretch the intermediate container to a base portion of the second mold and injecting high pressure air at a pressure of from 27.58 bar to 41.73 bar (400 psi to 600 psi) into the intermediate container to expand the intermediate container against the walls of the second mold to form the finished container;

• viii. directing a cooling fluid to an inner surface of the finished container.

2. The process of claim 1 or 2 wherein the PET resin has an intrinsic viscosity of from 0.72 dL/g to 0.86 dL/g.

3. The process of claim 1 or 2 wherein the preform is designed such that its thickness ratio relative to the finished container is in the range of from 2.0 to 7.5; preferably from 4.0 to 6.0.

5. The process of claim 1 or 2 wherein the preform is designed such that its thickness ratio relative to the finished container is in the range of from 3.4 to 4.2 in the shoulder portion of the container; from 3.8 to 4.5 in the barrel portion of the container; and from 2.4 to 2.8 in the base portion of the container.

6. The process of claim 1 or 2 wherein the preform is designed such that a density ratio of the finished container relative to the preform is in the range of from 1.025 and 1.049.

7. The process of claim 1 or 2 wherein the density ratio is greater than 1.049.

8. The process of claim 1 or 2 wherein the temperature of the preform when it is removed from the injection mold cavity is from 90° C. to 105° C.

9. The process of claim 1 or 2 wherein the preform, when it is removed from the injection mold cavity, exhibits a temperature gradient from an outside to an inside surface of not more than 5° C.

10. The process of claim 1 or 2 wherein the temperature of the preform when it is removed from the injection mold cavity is from about 80° C. to 110° C.

11. The process of claim 1 wherein the conditioning step ther temperature gradient in the specific areas is of as much as 30° C. preferably as much as 40° C.

12. The process of claim 1 or 2 wherein the temperature of the mold is from 73° C. to 250° C; preferably from 150° C. to 240° C ; more preferably from 160° C. to 230° C.

13. The process of claim 2 wherein the cooling fluid is air; preferably at a temperature of from 20° C. to 50° C.

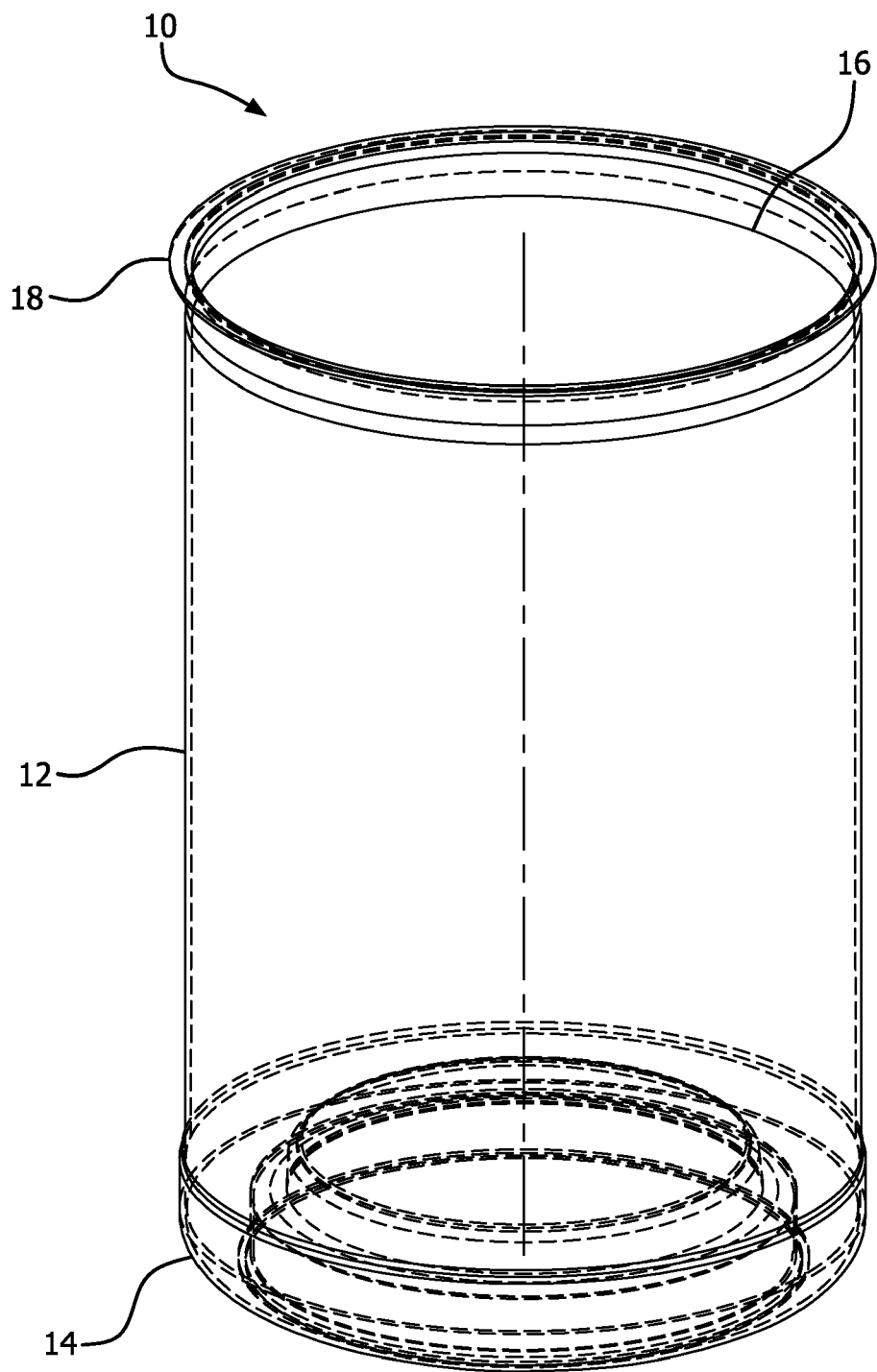


FIG. 1

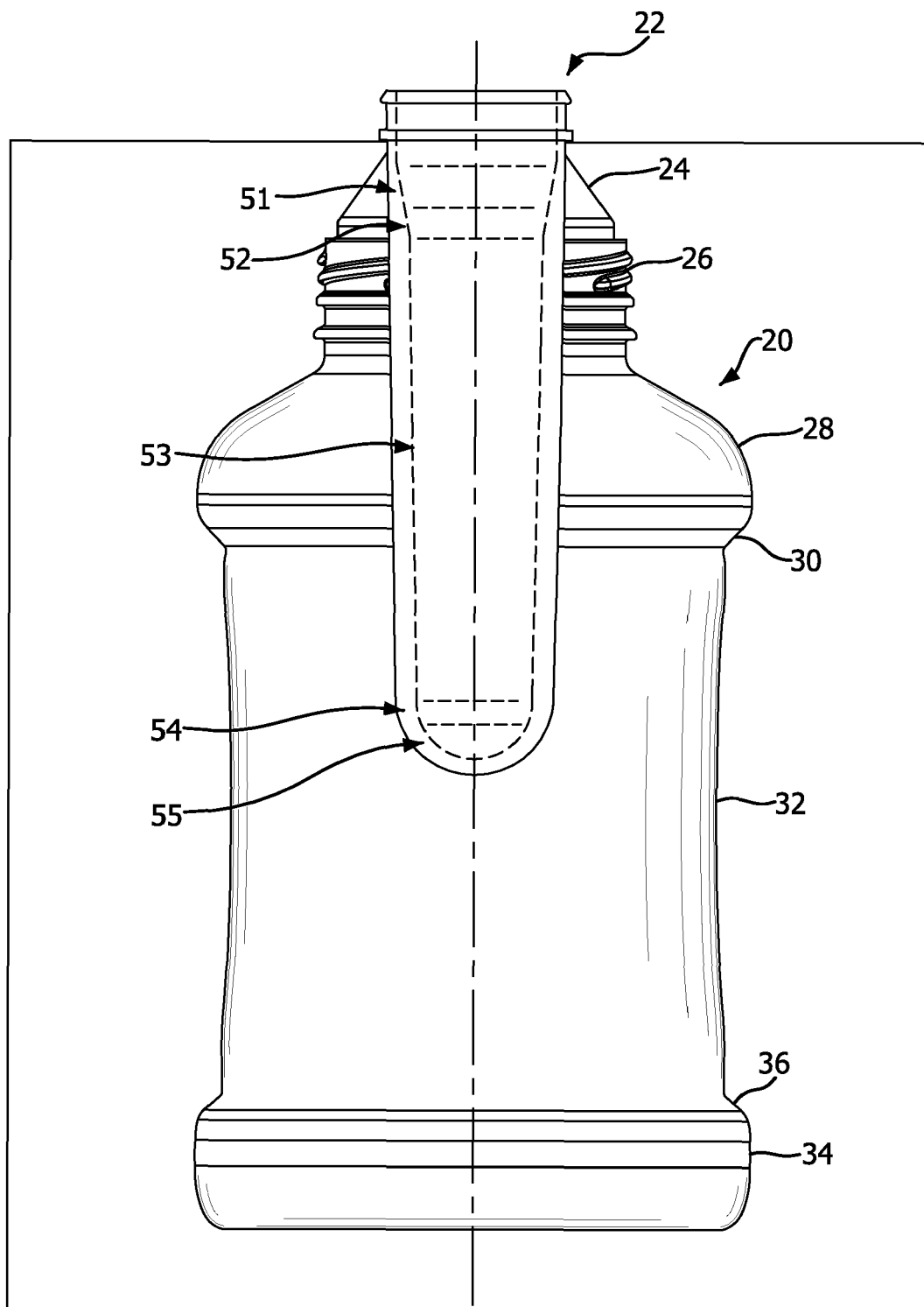


FIG. 2

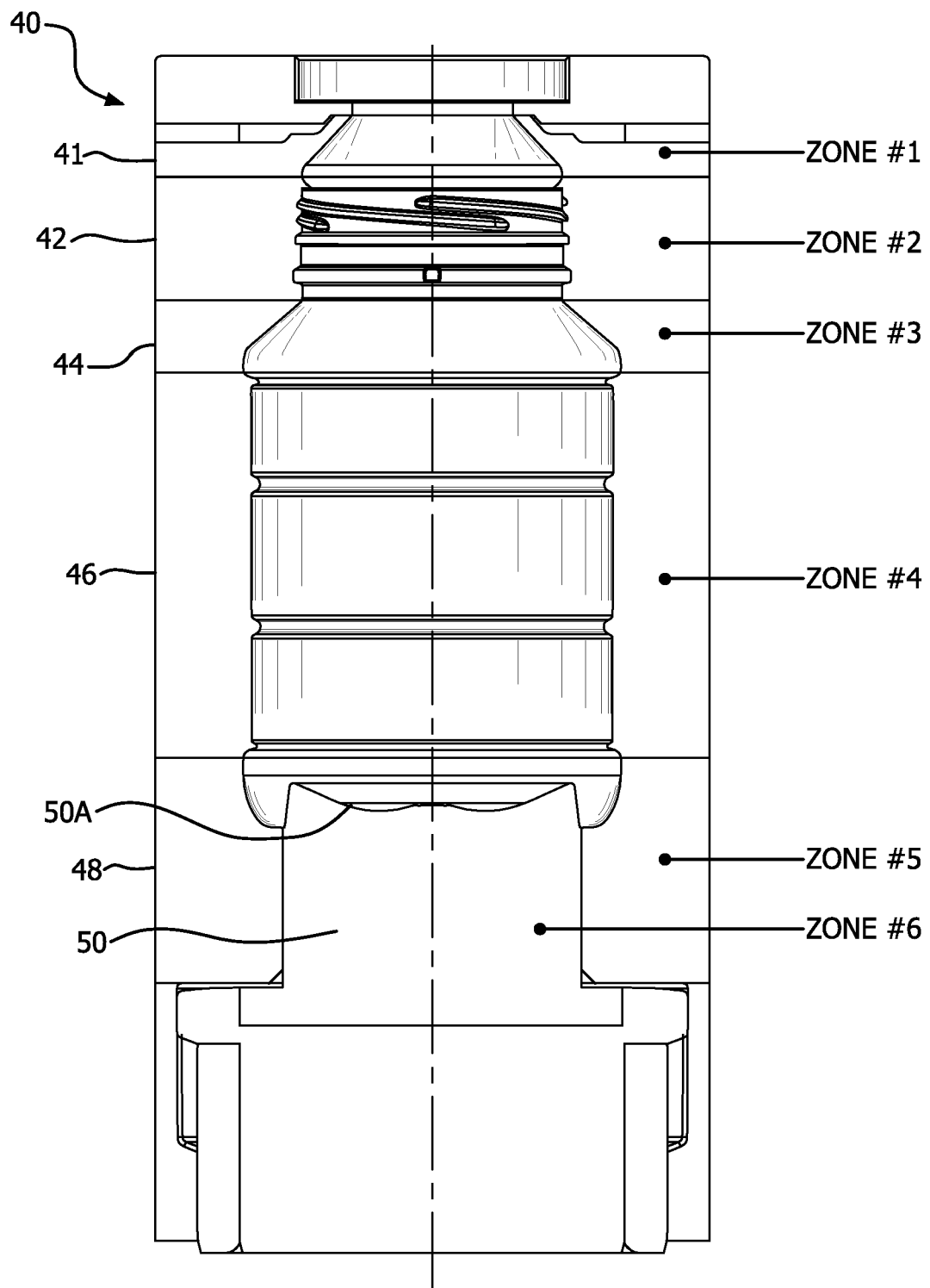


FIG. 3

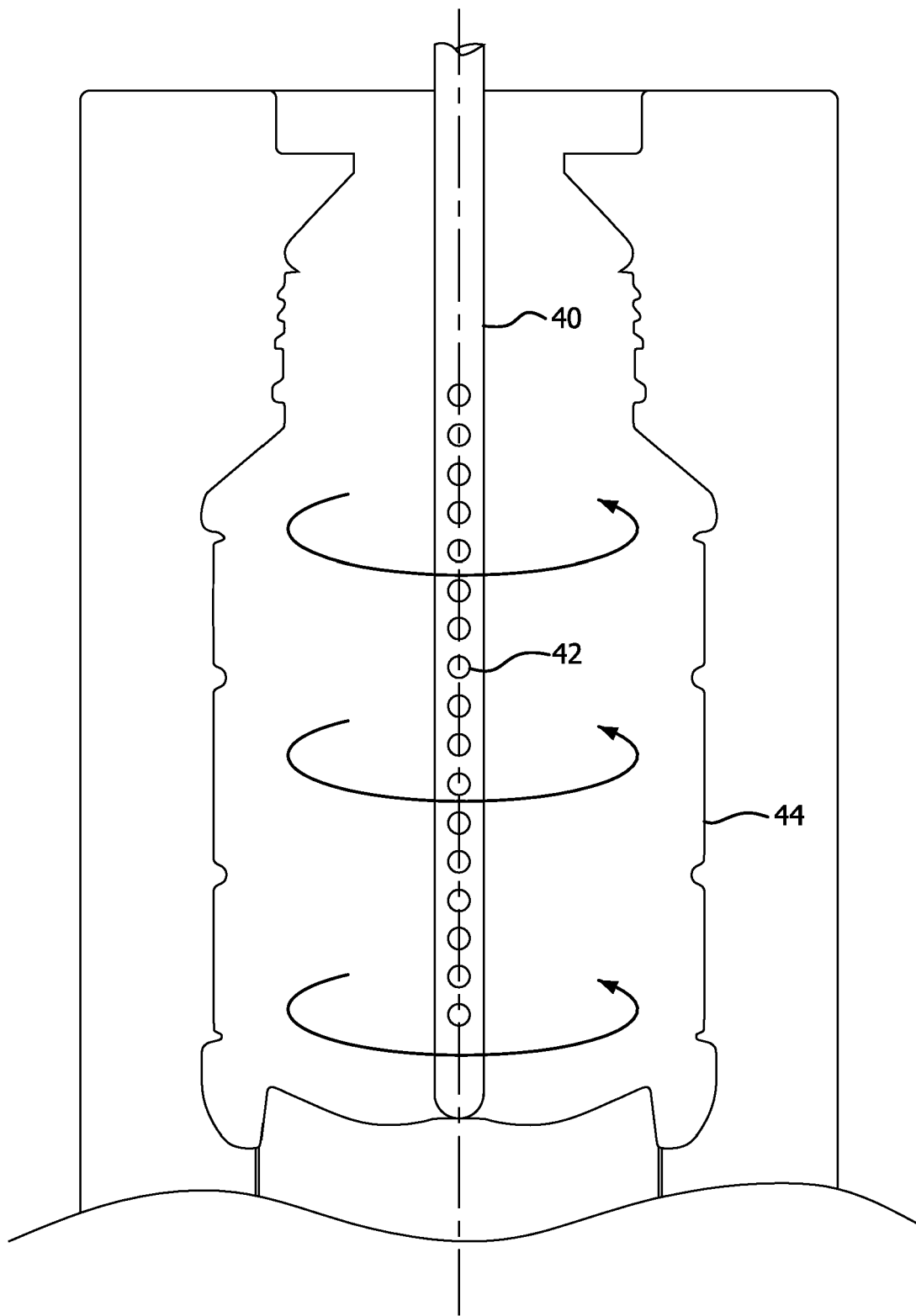
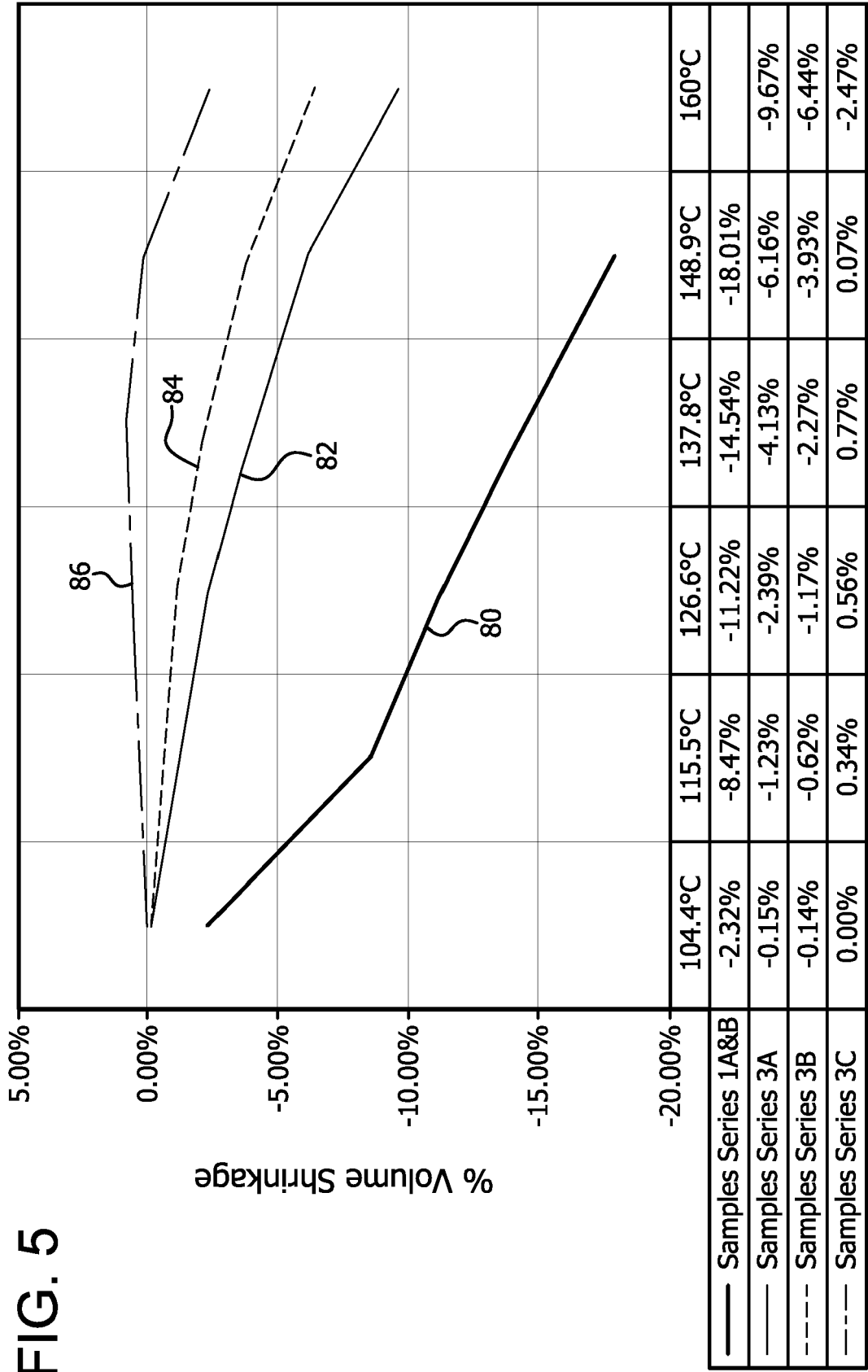
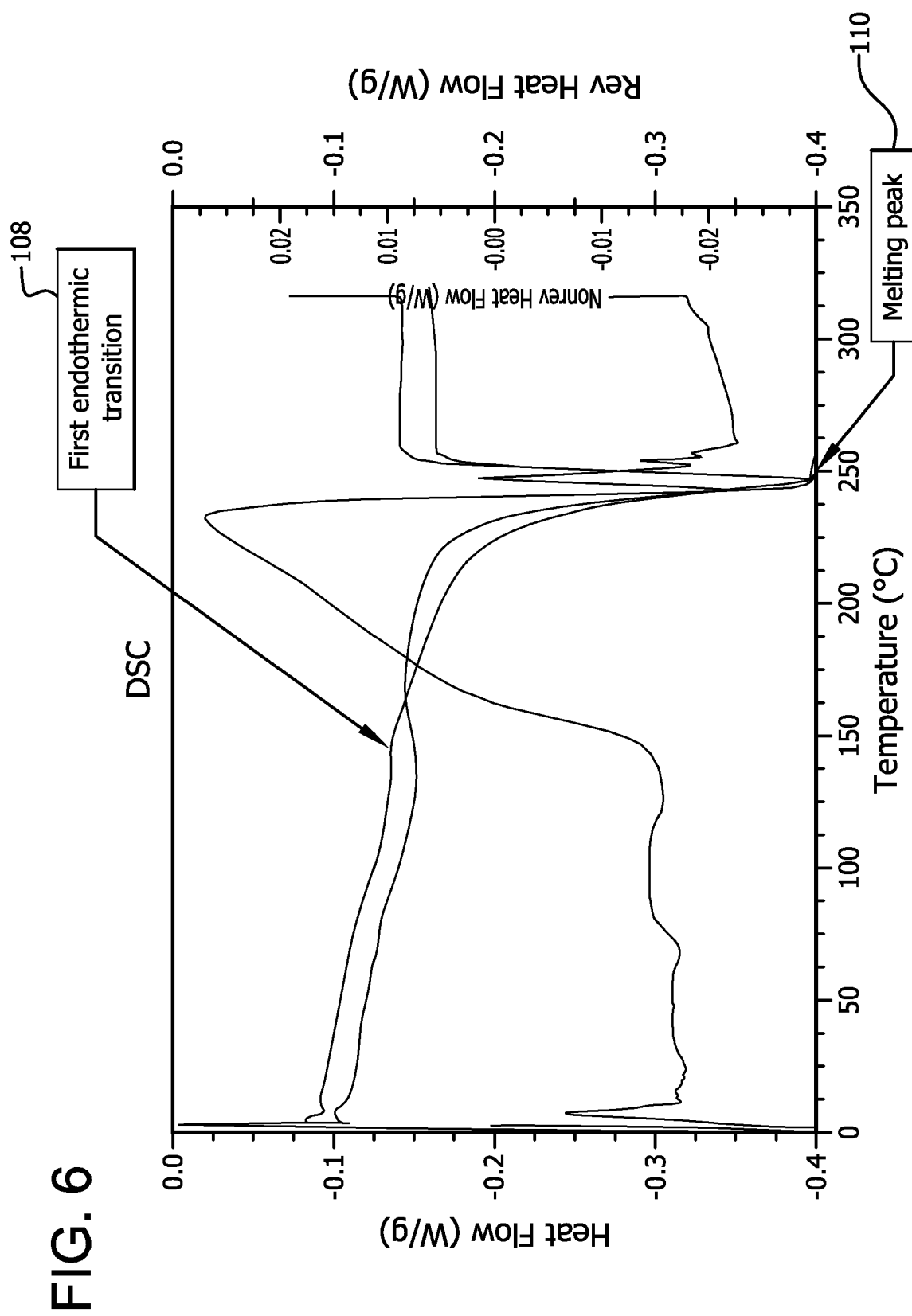
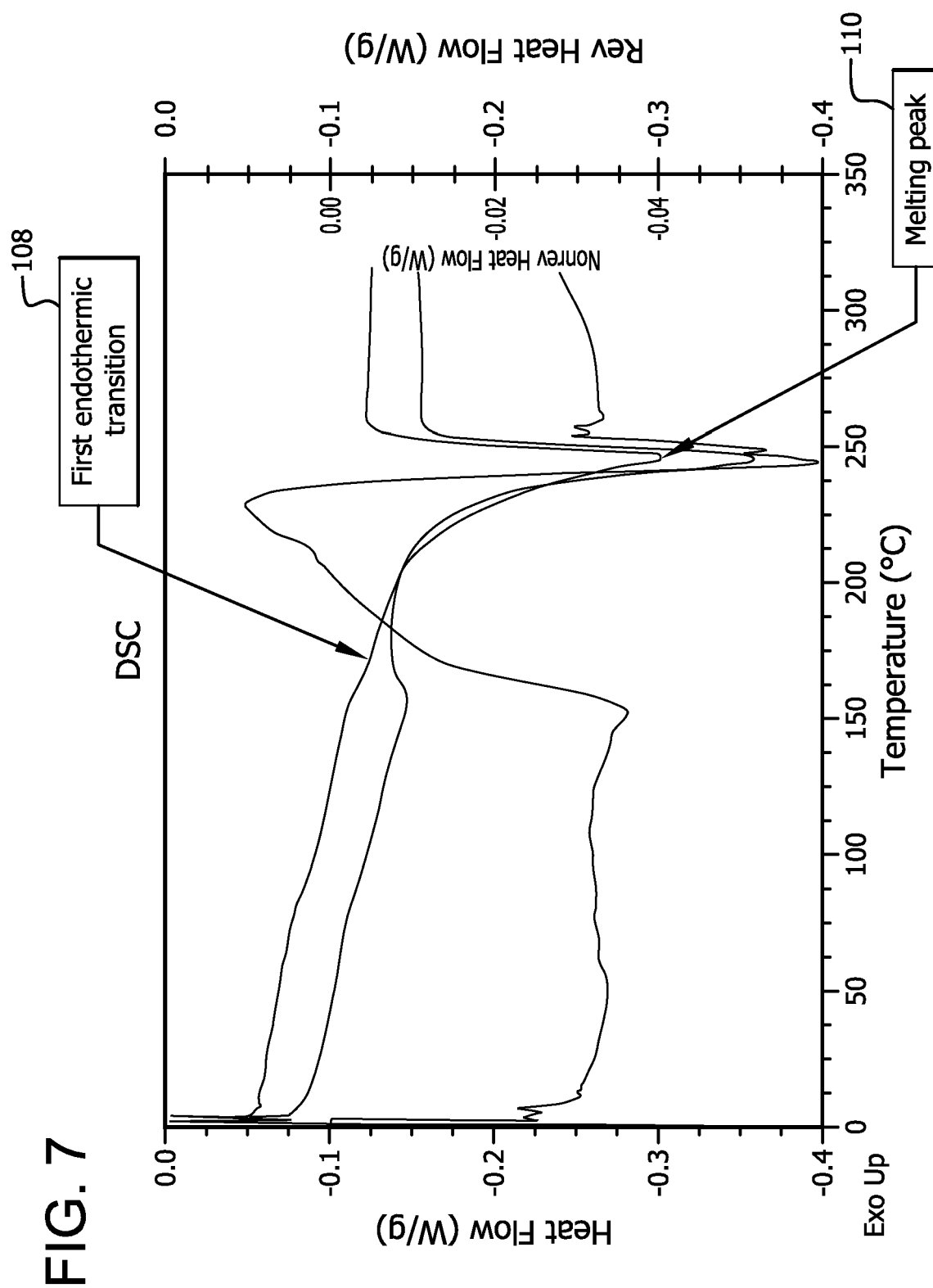
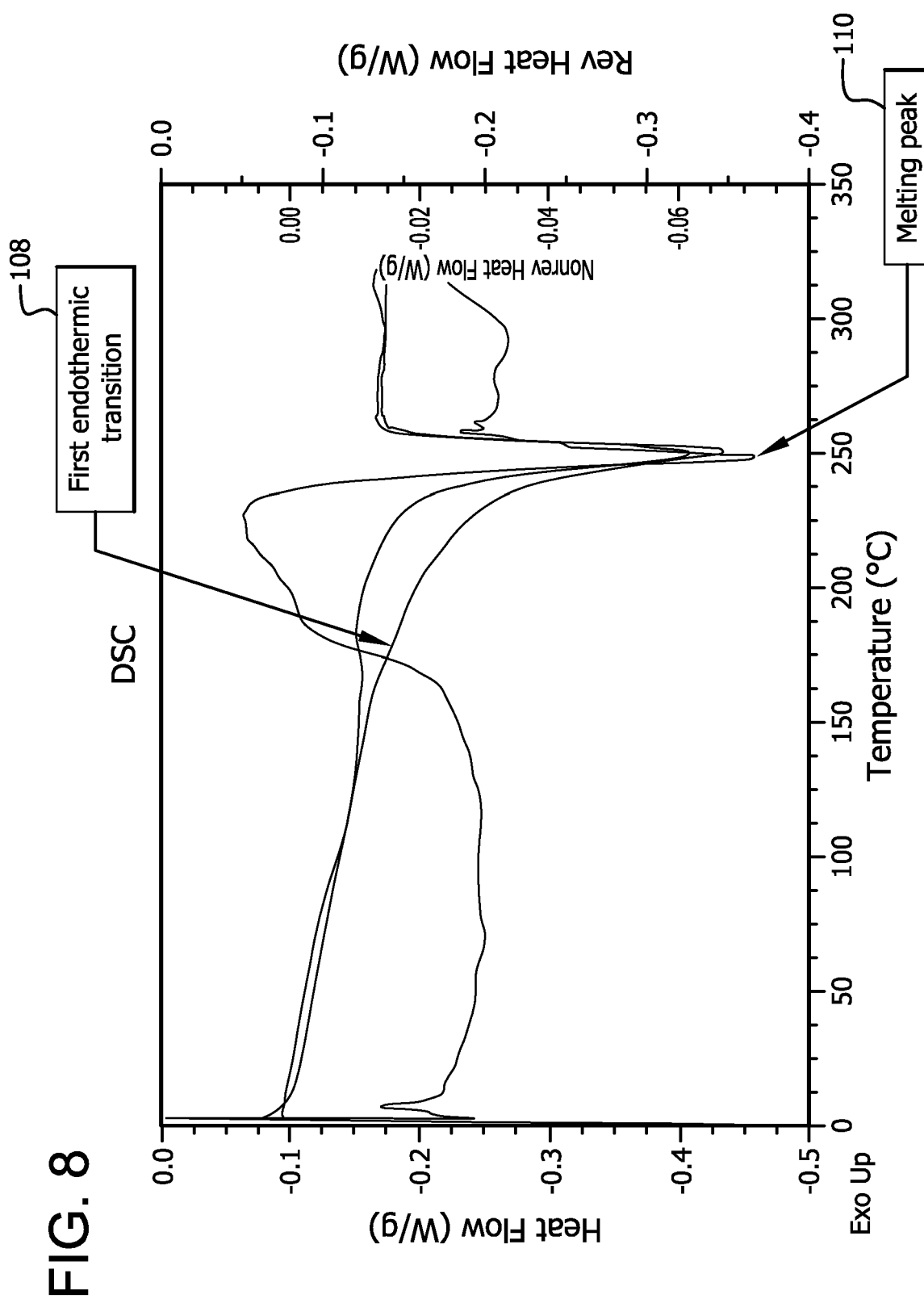


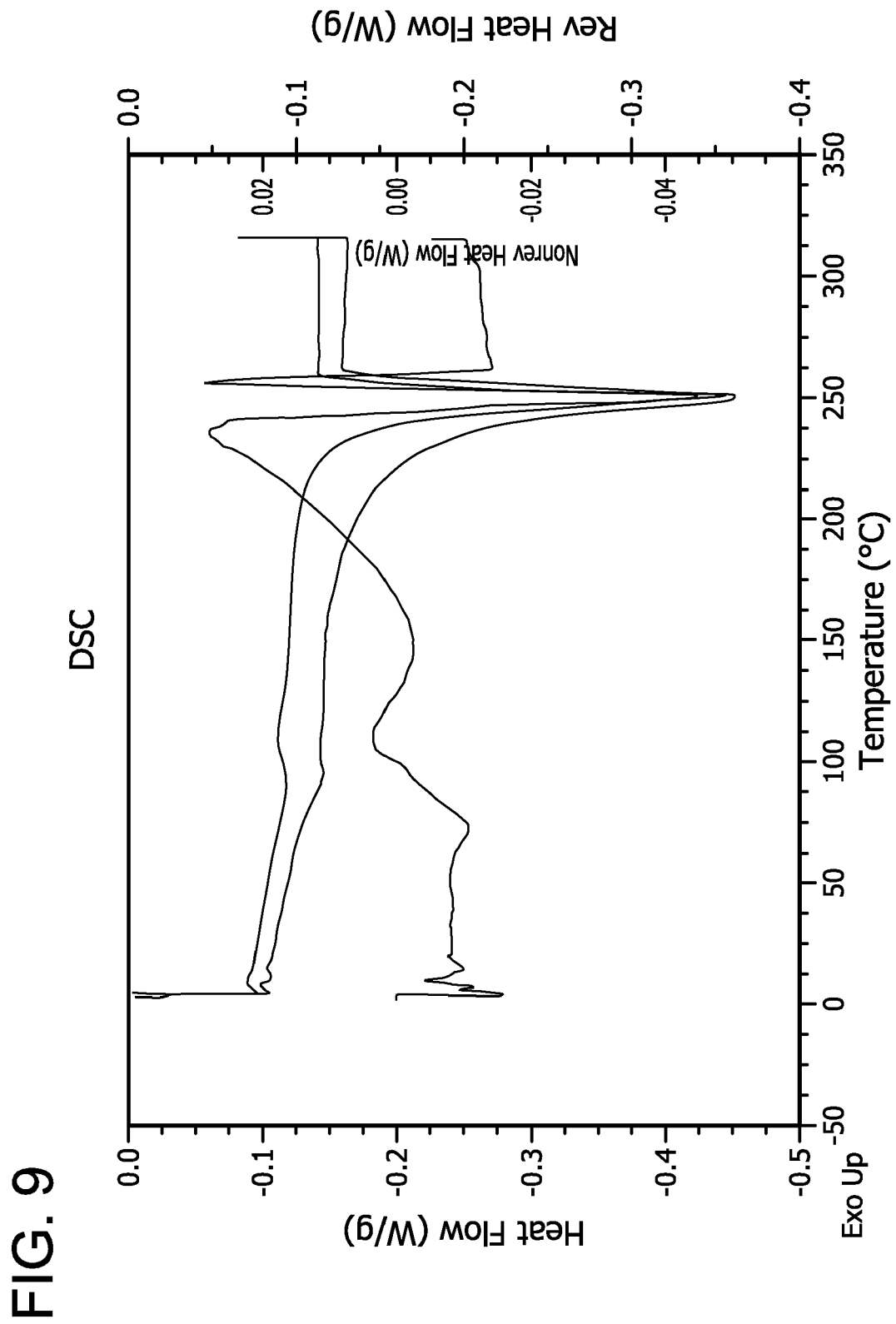
FIG. 4

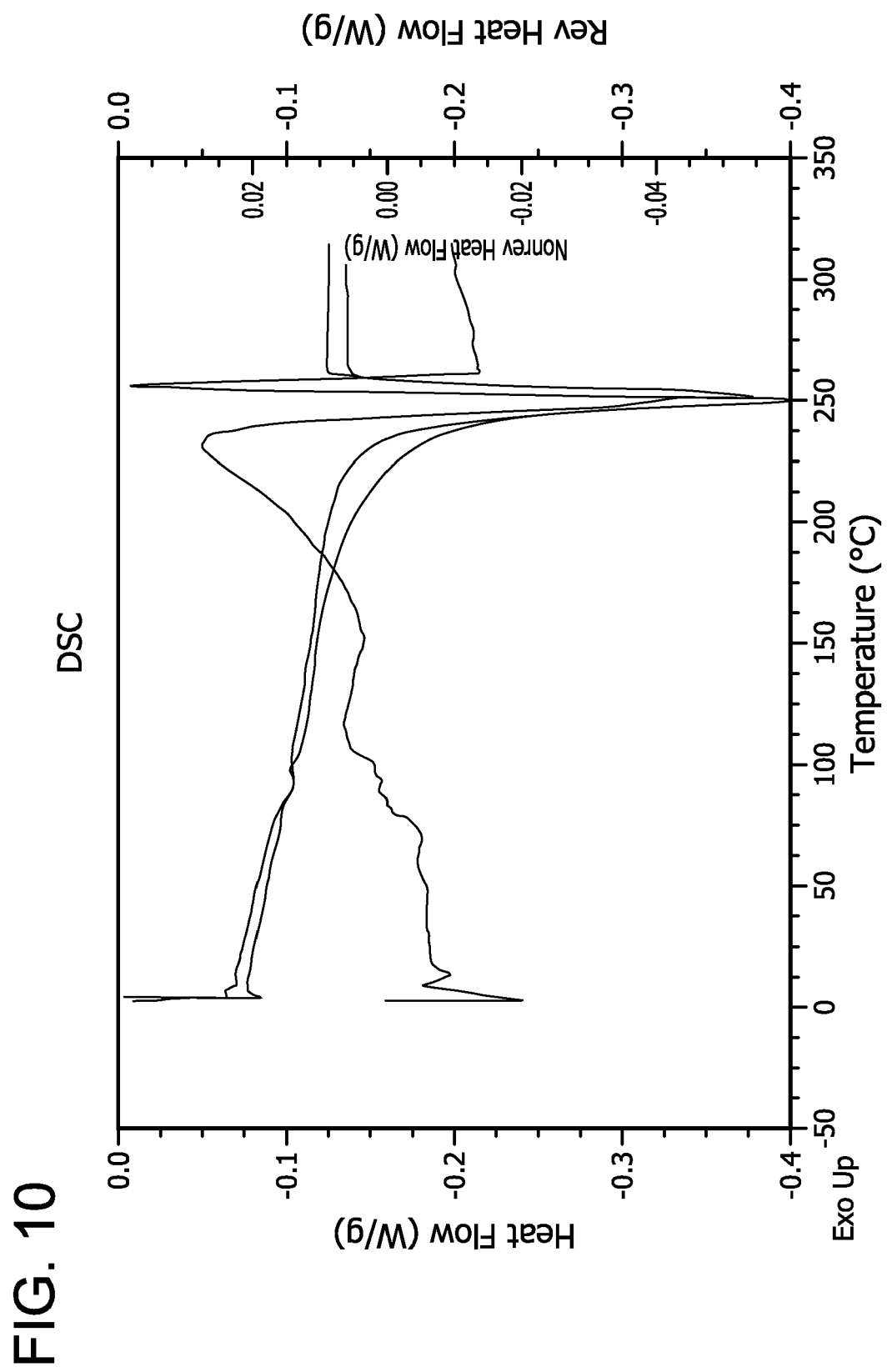












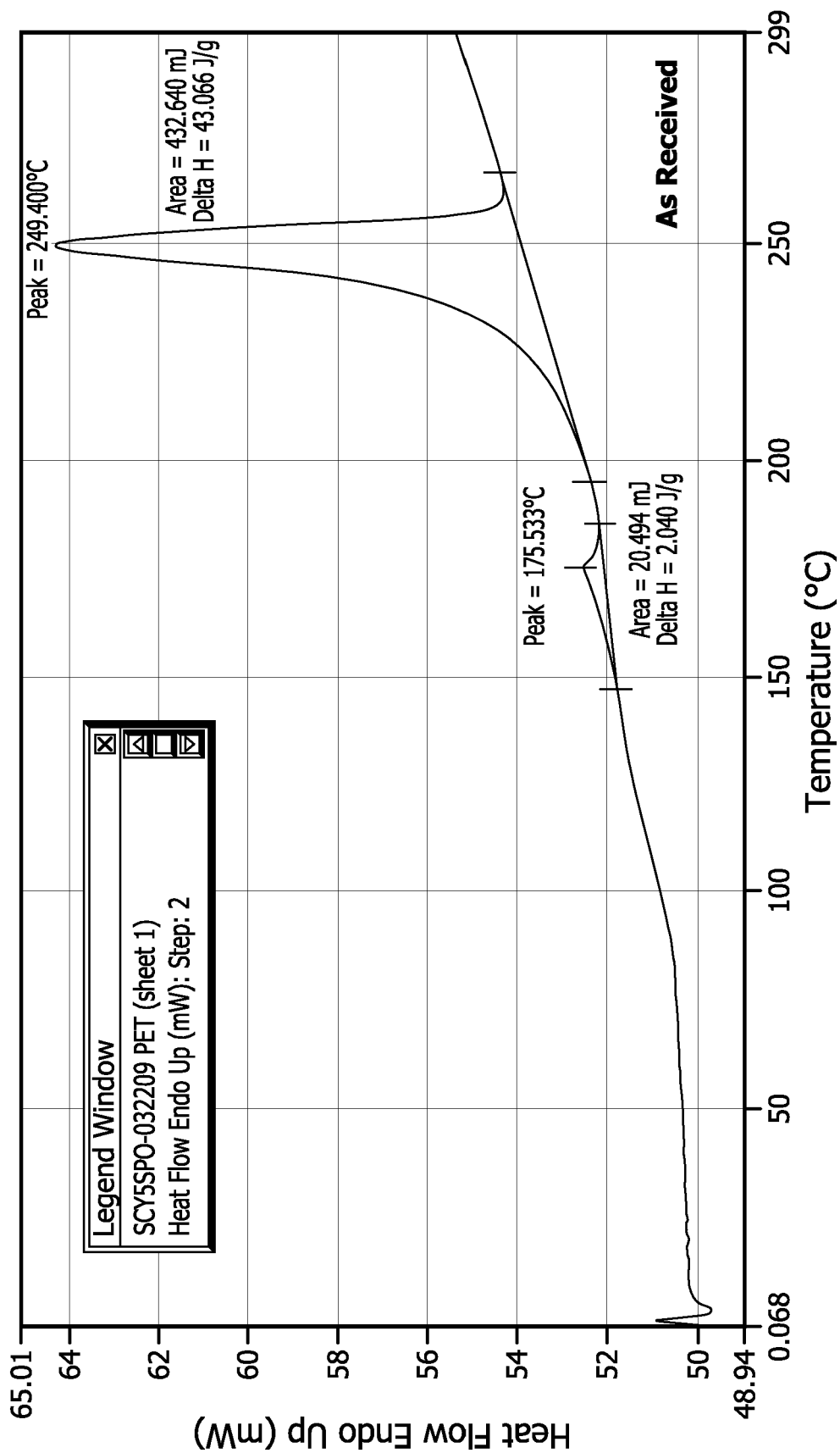


FIG. 11

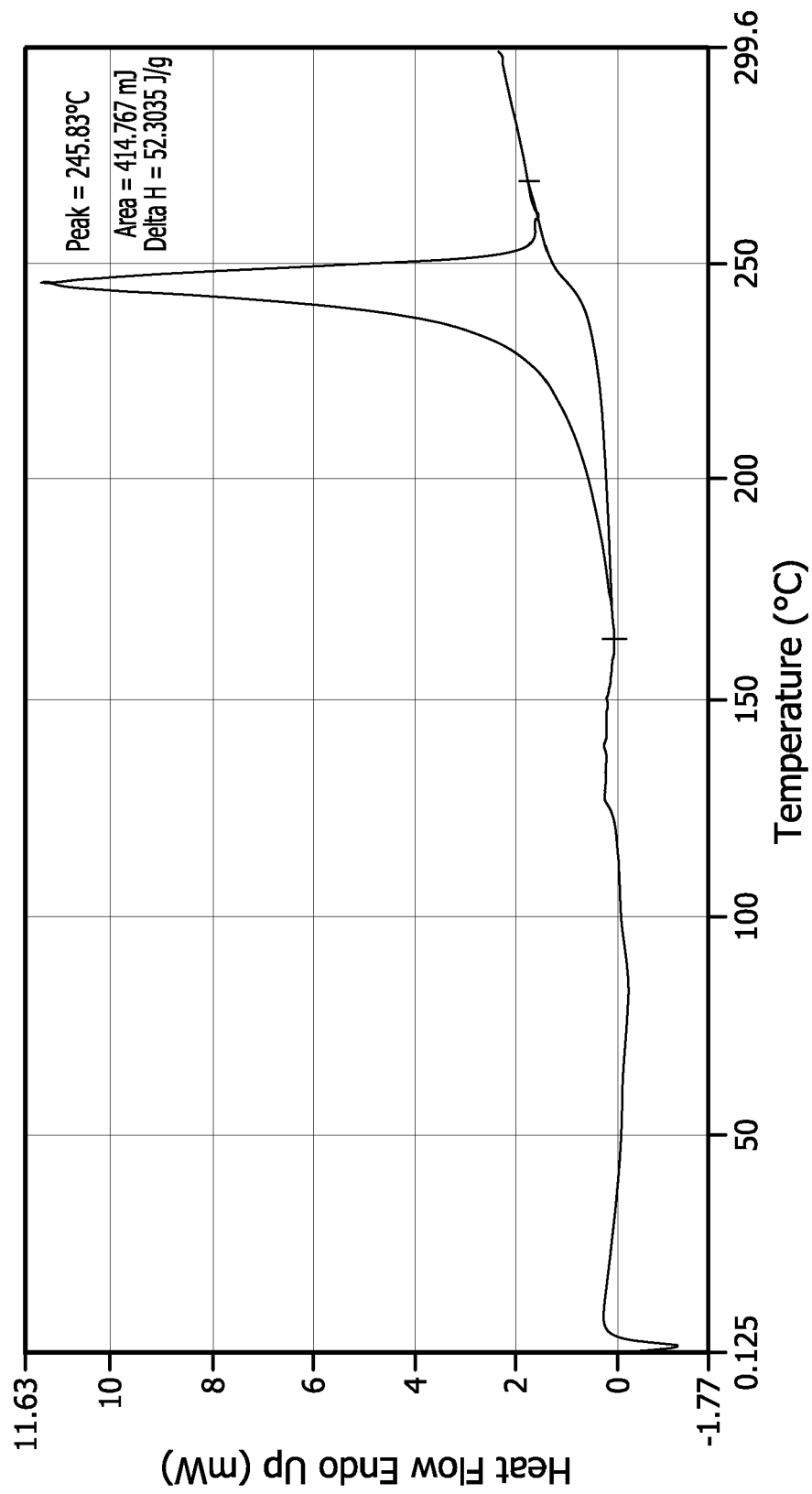


FIG. 12

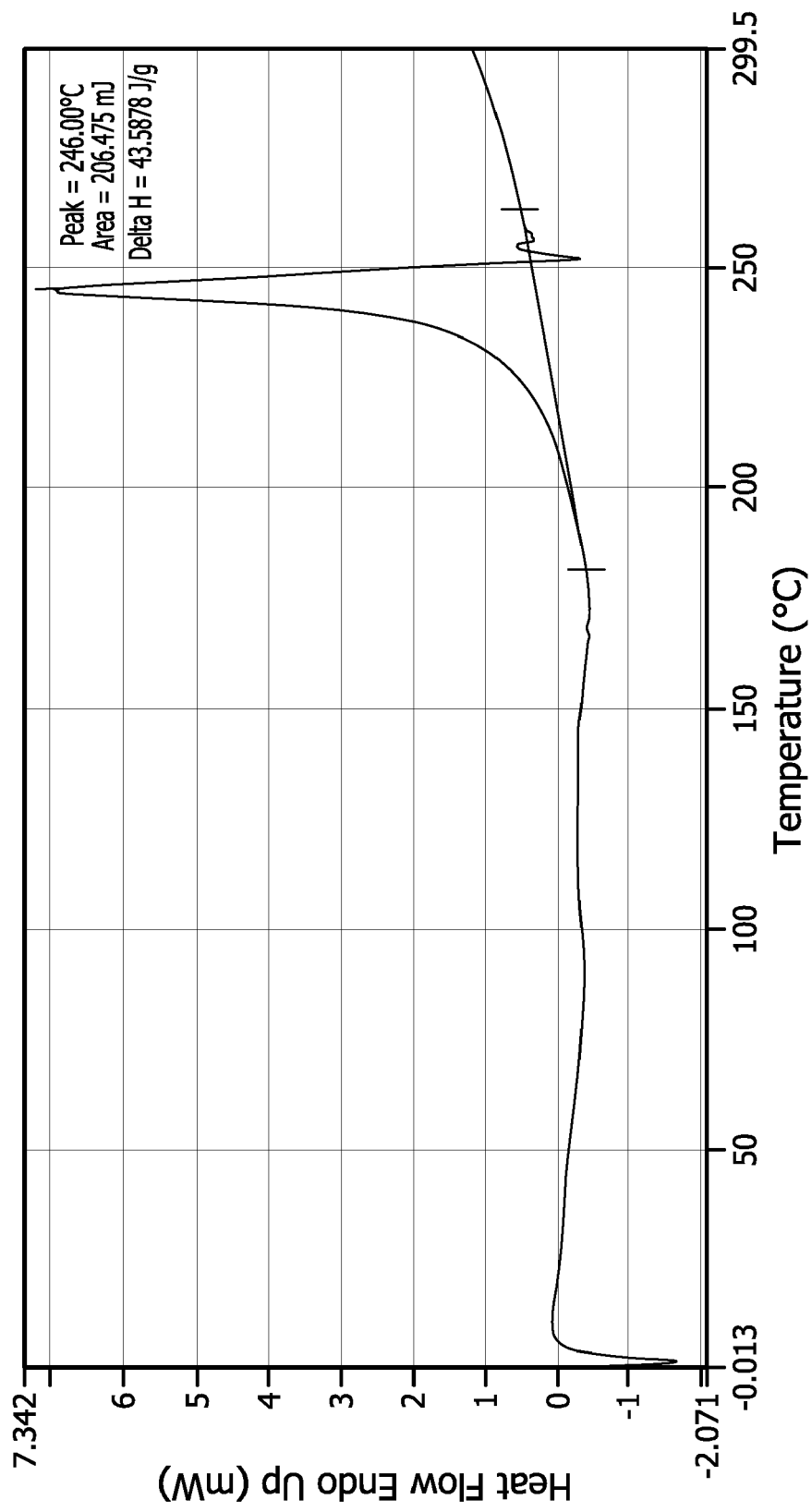


FIG. 13

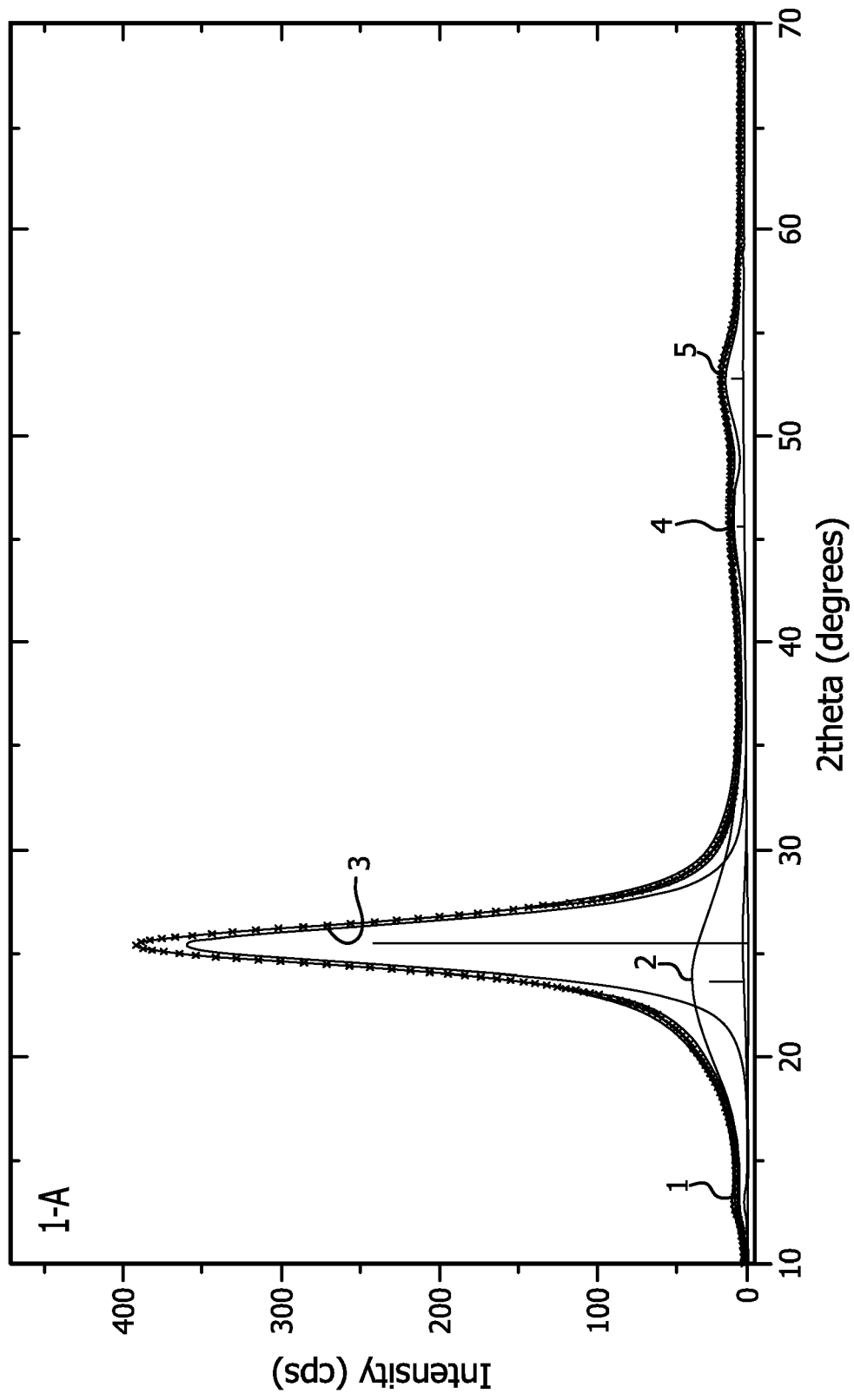


FIG. 14

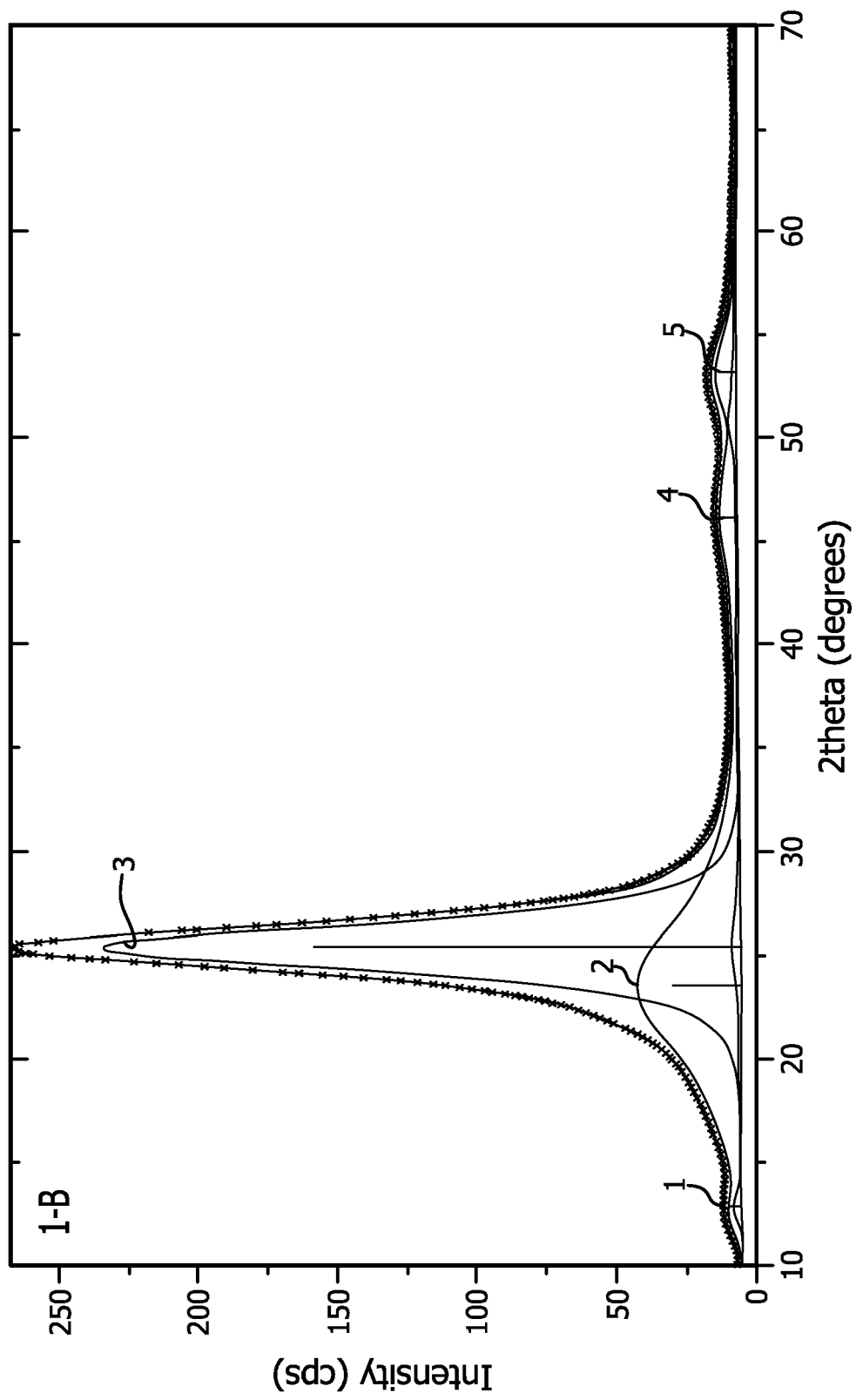


FIG. 15

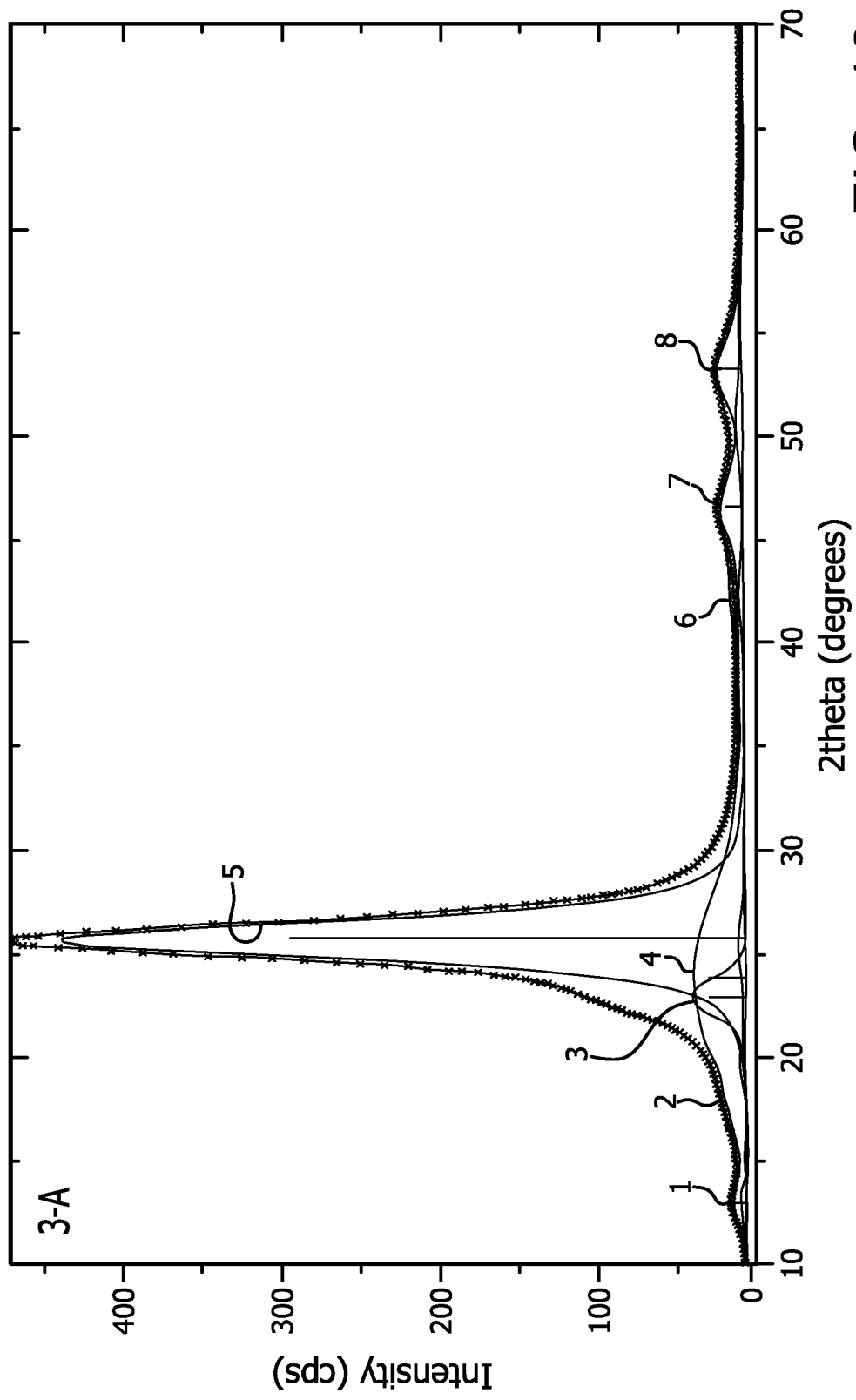


FIG. 16

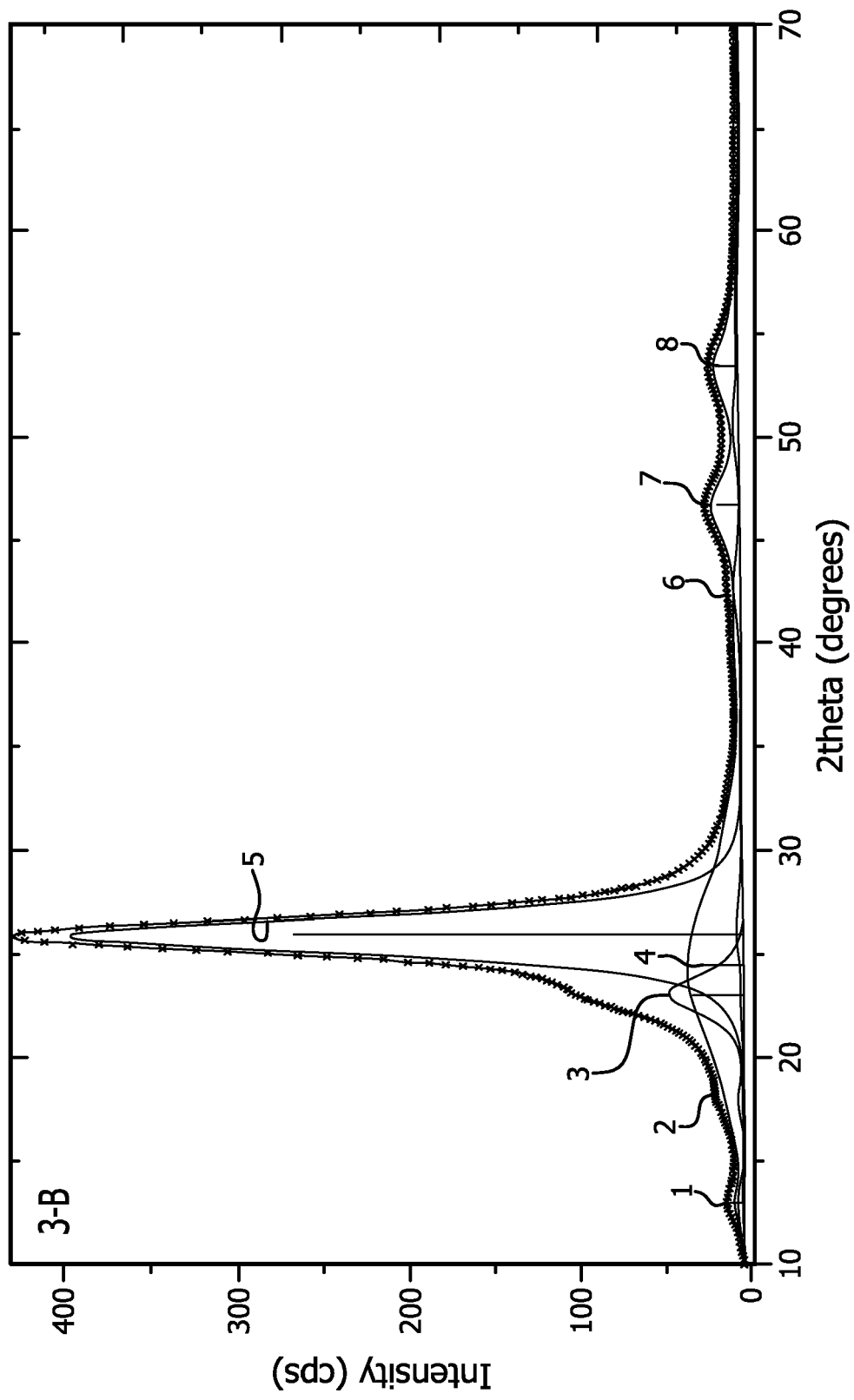


FIG. 17

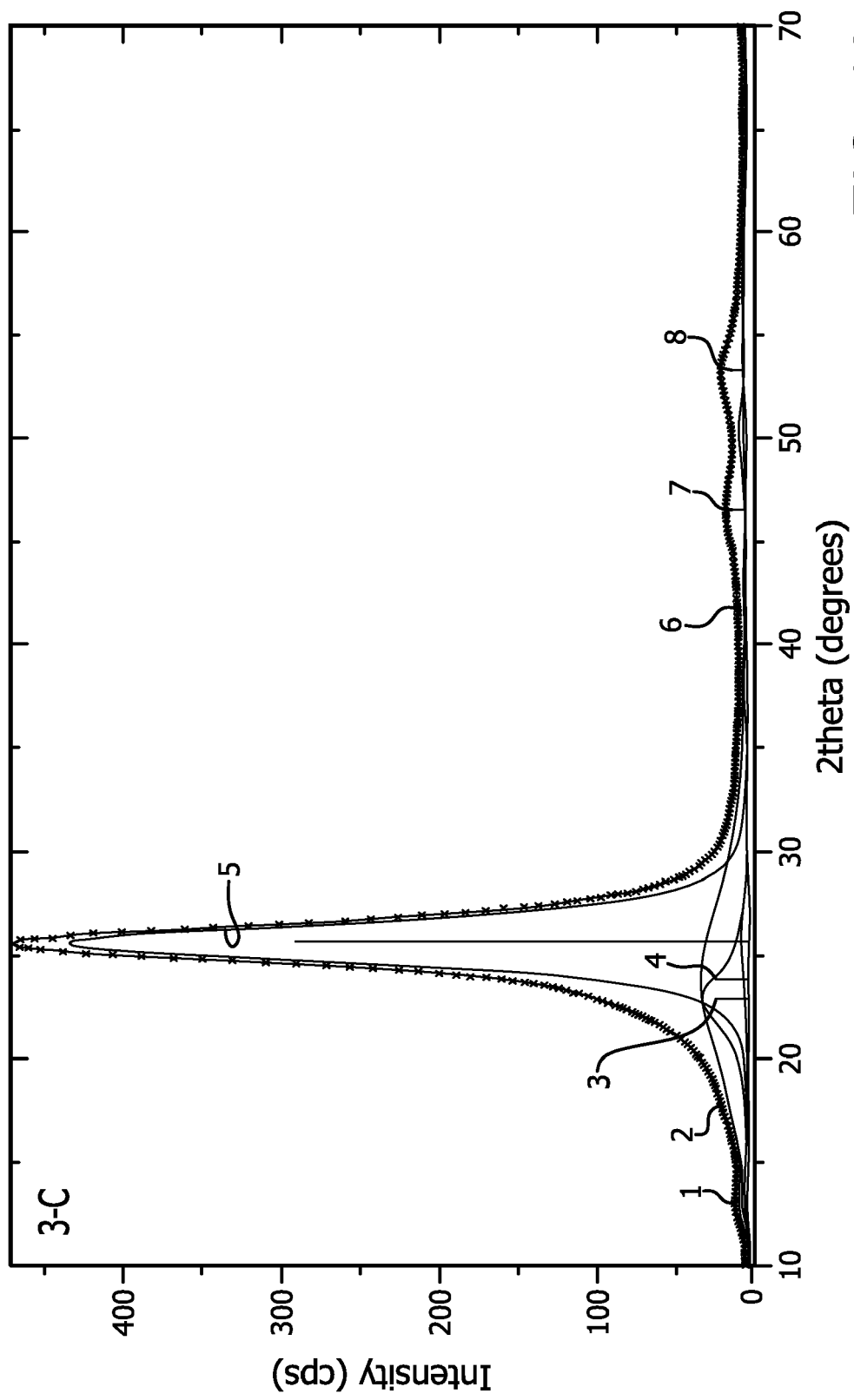


FIG. 18

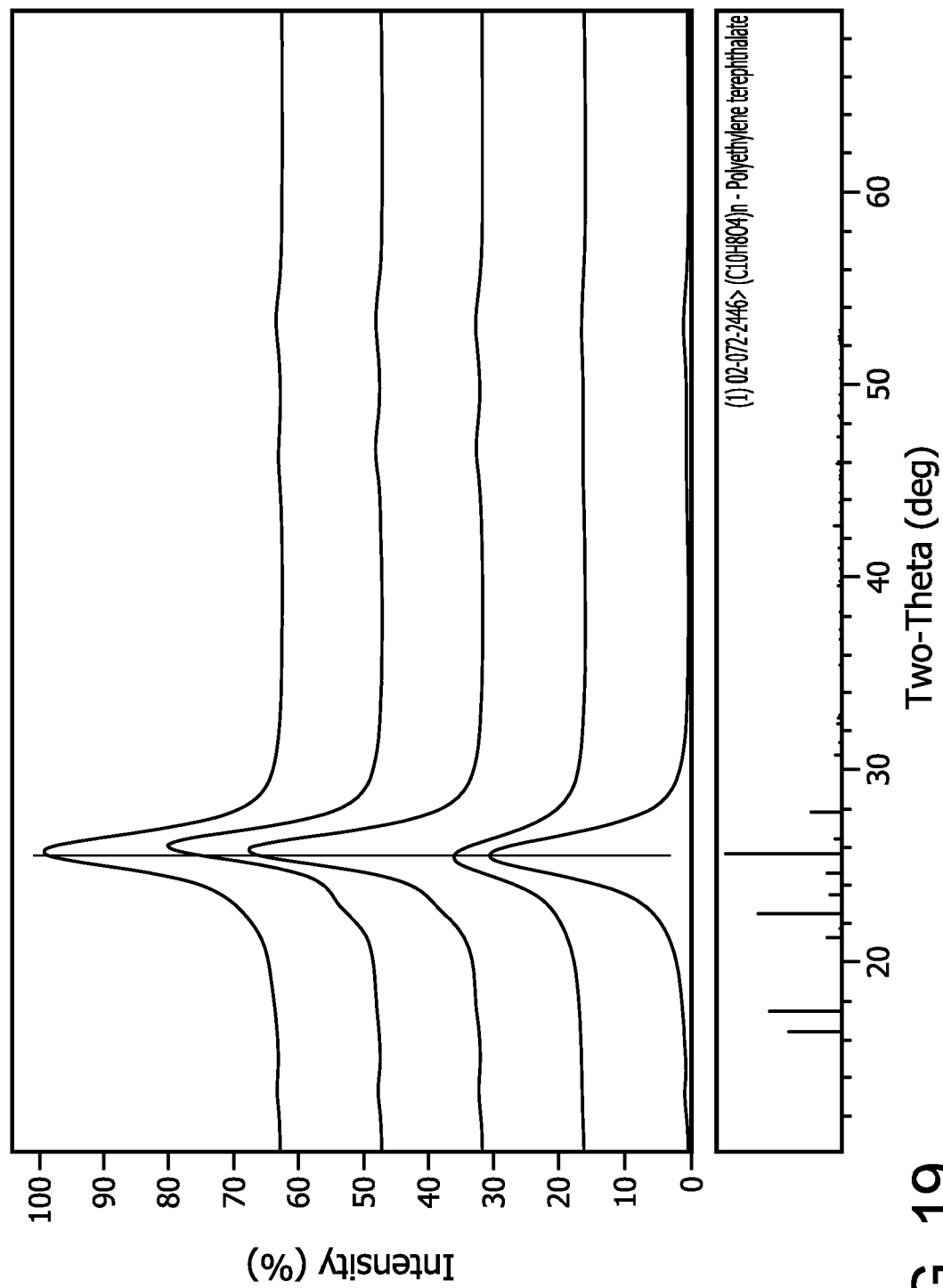


FIG. 19

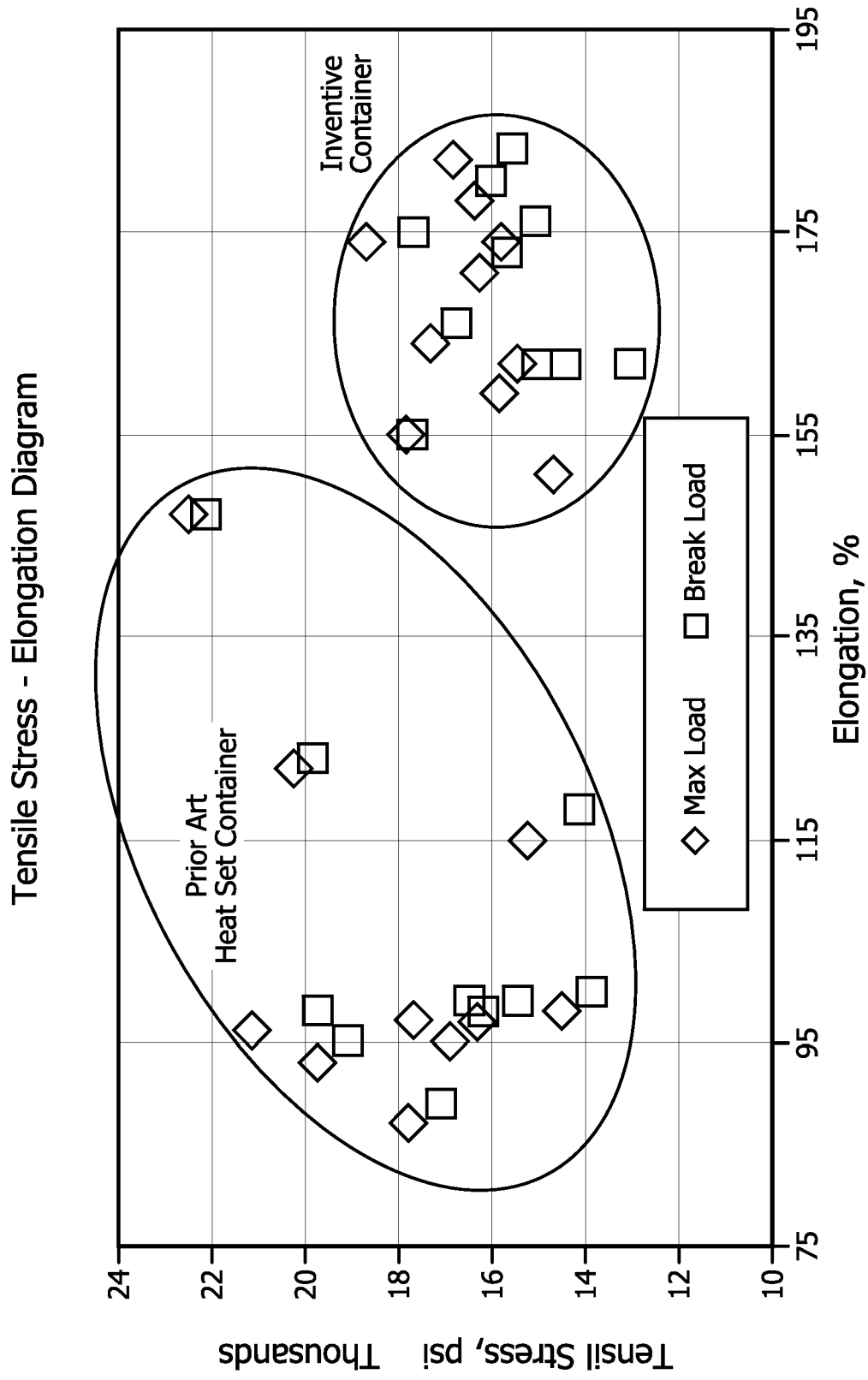


FIG. 20



EUROPEAN SEARCH REPORT

Application Number
EP 16 18 2977

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A,D	US 6 485 670 B1 (BOYD TIMOTHY J [US] ET AL) 26 November 2002 (2002-11-26) * figures 1-7 * * column 2, line 63 - column 3, line 5 * * column 3, line 63 - column 4, line 2 * * column 4, lines 10-15 * * column 4, line 18 - column 7, line 46 * * column 8, lines 5-16 * * column 8, line 35 - column 9, line 6 * * column 2, lines 1-18 * -----	1-13	INV. B29C49/48 B29C49/78 B29C49/18 B29C49/64 B29C49/16 ADD. B29C49/06 B29C49/12 B29C49/42
A	EP 1 155 807 A1 (YOSHINO KOGYOSHO CO LTD [JP]) 21 November 2001 (2001-11-21) * paragraphs [0002], [0015] - [0017], [0064] - [0067]; figures 1,3; examples 1,2 * -----	1-13	
A	GB 2 108 899 A (MITSUBISHI PLASTICS IND) 25 May 1983 (1983-05-25) * figures 1-4 * * page 1, lines 43-46,60 * * page 2, lines 8-9,18-20,55-65 * * page 3, lines 39-43 * * page 4, lines 7-23 * -----	1-13	TECHNICAL FIELDS SEARCHED (IPC) B29C B29K
A	US 4 790 741 A (TAKAKUSAKI NOBUYUKI [JP] ET AL) 13 December 1988 (1988-12-13) * figures 1,2,5 * * column 3, lines 49-58 * * column 4, lines 5-43 * * column 9, lines 30-44 * * column 13, line 26 - column 14, line 5 * -----	1-13	
A	US 2005/136149 A1 (KRISHNAKUMAR SUPPAYAN M [US] ET AL) 23 June 2005 (2005-06-23) * paragraphs [0020], [0021], [0023], [0029], [0031]; figures 2-5 * -----	1-13	
		-/--	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 29 November 2016	Examiner Baran, Norbert
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)



EUROPEAN SEARCH REPORT

 Application Number
 EP 16 18 2977

5

10

15

20

25

30

35

40

45

1

50

55

EPO FORM 1503 03.82 (P04C01)

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	EP 0 860 265 A1 (NISSEI ASB MACHINE CO LTD [JP]) 26 August 1998 (1998-08-26) * figures 1,3,4 * * column 2, lines 28-31,53-55 * * column 3, lines 14-27 * * column 5, lines 31-33 * * column 6, lines 47-50 * * column 7, lines 29-39 * * column 7, line 56 - column 8, line 11 * * column 8, line 19 - column 9, line 22 * * column 10, lines 9-32 * * column 10, line 49 - column 11, line 20 * * column 13, lines 6-47 * * column 14, lines 29-58 * * column 16, line 10 - column 17, line 2 * -----	1-13	TECHNICAL FIELDS SEARCHED (IPC)
A,D	US 5 562 960 A (SUGIURA HOROAKI [JP] ET AL) 8 October 1996 (1996-10-08) * claims 1,4,5 * * column 2, line 39 - column 3, line 67 * * column 4, lines 27-50 * * column 5, lines 4-16 * -----	1-13	
A	EP 0 559 103 A1 (NISSEI ASB MACHINE CO LTD [JP]) 8 September 1993 (1993-09-08) * figures 2-7 * * column 2, line 49 - column 3, line 15 * * column 6, line 9 - column 11, line 42 * -----	1-13	
A,P	WO 2011/037792 A1 (GRAHAM PACKAGING LC L P [US]; SCHNEIDER MARK D [US]; SILVERS KERRY W []) 31 March 2011 (2011-03-31) * claims 1-22,29,34; figures 1-17; tables 1,2,5 * * page 8, line 26 - page 12, line 22 * * page 16, lines 1-9 * ----- -/--	1-13	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		29 November 2016	Baran, Norbert
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



EUROPEAN SEARCH REPORT

Application Number
EP 16 18 2977

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 5 829 614 A (COLLETTE WAYNE N [US] ET AL) 3 November 1998 (1998-11-03) * figures 2-7 * * column 3, lines 49-63 * * column 6, lines 47-59 * * column 7, lines 10-35 * * column 8, line 59 - column 11, line 36 * -----	1-13	
			TECHNICAL FIELDS SEARCHED (IPC)
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 29 November 2016	Examiner Baran, Norbert
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 1
EPO FORM 1503 03/02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 16 18 2977

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

29-11-2016

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6485670 B1	26-11-2002	AT 258849 T	15-02-2004
		BR 0015444 A	16-07-2002
		CA 2389988 A1	17-05-2001
		DE 60008135 D1	11-03-2004
		DE 60008135 T2	22-07-2004
		EP 1232055 A1	21-08-2002
		MX PA02004629 A	10-09-2004
		US 6485670 B1	26-11-2002
		US 2002076462 A1	20-06-2002
EP 1155807 A1	21-11-2001	WO 0134370 A1	17-05-2001
		AU 758920 B2	03-04-2003
		AU 1554001 A	12-06-2001
		CA 2360792 A1	07-06-2001
		CN 1338987 A	06-03-2002
		CN 1616307 A	18-05-2005
		DE 60018042 D1	17-03-2005
		DE 60018042 T2	29-12-2005
		EP 1155807 A1	21-11-2001
GB 2108899 A	25-05-1983	KR 20060128062 A	13-12-2006
		TW 505597 B	11-10-2002
		US 2004065984 A1	08-04-2004
		WO 0139956 A1	07-06-2001
		AU 554049 B2	07-08-1986
		AU 1232483 A	13-09-1984
		CA 1188469 A	11-06-1985
		DE 3241571 A1	19-05-1983
		FR 2516013 A1	13-05-1983
US 4790741 A	13-12-1988	GB 2108899 A	25-05-1983
		IT 1154544 B	21-01-1987
		JP H0351568 B2	07-08-1991
		JP S5881131 A	16-05-1983
		NZ 202293 A	08-11-1985
		US 4550007 A	29-10-1985
		AU 1987288 A	09-03-1989
		CA 1292107 C	19-11-1991
		EP 0328653 A1	23-08-1989
US 2005136149 A1	23-06-2005	US 4790741 A	13-12-1988
		WO 8901400 A1	23-02-1989
		CA 2412364 A1	27-05-2003
		EP 1314535 A1	28-05-2003
		JP 2003231171 A	19-08-2003
		MX PA02011666 A	03-09-2004

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 16 18 2977

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

29-11-2016

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		NZ 522763 A	29-10-2004
		NZ 534759 A	28-04-2006
		US 2003098526 A1	29-05-2003
		US 2005136149 A1	23-06-2005
EP 0860265	A1 26-08-1998	CN 1191797 A	02-09-1998
		DE 69805347 D1	20-06-2002
		DE 69805347 T2	16-01-2003
		EP 0860265 A1	26-08-1998
		ES 2176834 T3	01-12-2002
		JP 3760045 B2	29-03-2006
		JP H10286874 A	27-10-1998
		KR 100388363 B1	19-08-2003
		US 6080353 A	27-06-2000
US 5562960	A 08-10-1996	US 5562960 A	08-10-1996
		US 5747130 A	05-05-1998
		US 5928742 A	27-07-1999
EP 0559103	A1 08-09-1993	DE 69310416 D1	12-06-1997
		DE 69310416 T2	26-02-1998
		EP 0559103 A1	08-09-1993
		JP H0813498 B2	14-02-1996
		JP H06143392 A	24-05-1994
		US 5389332 A	14-02-1995
WO 2011037792	A1 31-03-2011	EP 2480395 A1	01-08-2012
		ES 2541840 T3	27-07-2015
		US 2011070388 A1	24-03-2011
		WO 2011037792 A1	31-03-2011
US 5829614	A 03-11-1998	AT 157927 T	15-09-1997
		AU 679186 B2	26-06-1997
		AU 4663793 A	31-01-1994
		CA 2139741 A1	20-01-1994
		CN 1089226 A	13-07-1994
		DE 69313862 D1	16-10-1997
		DE 69313862 T2	22-01-1998
		EP 0653982 A1	24-05-1995
		SK 1595 A3	13-09-1995
		US 5829614 A	03-11-1998
		US 6372318 B1	16-04-2002
		US 2002150703 A1	17-10-2002
		US 2005271843 A1	08-12-2005
		WO 9401269 A1	20-01-1994

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 4476170 A [0010]
- US 4512948 A [0010]
- US 4522779 A [0010]
- US 4535025 A [0010]
- US 4603066 A [0010]
- US 4713270 A [0010]
- US 4839127 A [0010]
- US 4891178 A, Jabarin [0010]
- US 5562960 A [0011]
- US 5501590 A [0011]
- US 6485669 B [0012]
- US 6485670 B [0012]
- US 6514451 B [0012]
- US 6749415 B [0012]
- US 6767197 B [0012]
- US 7033656 B [0013]
- US 4233022 A [0014]
- US 6841117 B [0015]
- US 709302 A [0042]
- US 20110204067 A [0042]

Non-patent literature cited in the description

- **MARIA CRISTINA RIGHETTI ; MARIA LAURA DI LORENZO.** *Vitrification and Devitrification of the Rigid Amorphous Fraction in poly(ethylene terephthalate)*, 2009 [0007]